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DEVELOPMENT OF DIRECT CURRENT PLASMA ANALYTICAL METHODS FOR USE IN CANADIAN GOLD MINING AND MILLING OPERATIONS (UP-W-223)

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for

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ABSTRACT

This report reviews the applicability of Direct Current Plasma Emission spectroscopy (DCP) for the analysis of gold and other important metals present in gold milling solutions. The analytical performance of DC plasma spectroscopy and the method development for this application are described. Optimum analysis conditions and analyte lines are recommended. Comparative analyses with the atomic absorption spectroscopy methods,which are more commonly used in the mining industry, are presented. The results of hydrometallurgical mass balance calaculations confirm the usefulness of DC plasma spectroscropy for the determination of precious and other metals in gold milling solutions.

RÉSUMÉ

Ce rapport presente l'utilité de la spectroscopie à plasma à courant direct (DCP) dans l'analyse de l'or et autres métaux importants provenant des moulins à or. La performance analytique de la technique ainsi que le développement de la méthode sont décrits. Les conditions optimales et les longueurs d'onde analytiques sont recommandées. Les resultats d'analyse par spectroscopie à plasma à courant direct (DCP) et absorption atomique (AA) sont comparés. Les calculs du bilan de masse hydrométallurgique confirment l'efficacité de la technique dans l'analyse des métaux précieux et autres métaux d'importance à l'industrie aurifère.

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1.0 INTRODUCTION

Direct current plasma emission spectrocopy (DCP) has shown rapid acceptance in recent years as a routine, cost effective instrumental method of atomic analysis. Its high precision and accuracy, low detection limits, wide linear range, freedom from chemical and spectral interfence, manageable matrix and background effects, in addition to its qualitative and multi-element capabilities, make DC plasma spectroscopy an attractive alternative to traditional atomic absorption spectroscopy and inductively coupled plasma spectroscopy. Consequently, DCP is finding wide and diverse applications in a variety of fields including waste water analysis, geochemistry, energy, mining and metallurgy.

Although the application of DC plasma spectroscopy to the analysis of metals in gold milling solutions exists, there is very little literature specific to the use of DCP. Atomic absorption methods commonly used in the gold mining and milling industry are not necessarily transferable or applicable to direct usage in DCP.

For this reason, Witteck Development Inc. submitted an unsolicited proposal to the Department of Supply and Services to develop DC plasma spectroscopy methods for use in Canadina gold

mining and milling operations. This report describes the analytical methods developed to monitor gold and several other important metals including Ag, Fe, Cu, Zn, As and Hg in solutions from representative gold milling operations. This report also summarizes the relevant literature which is applicable to the analysis of gold milling solutions by atomic spectroscopy. Particular emphasis has been placed on fundamental concepts and analytical studies which have been performed using atomic absorption and emission methods that are applicable to the analysis of gold milling solutions.

The experimental work that is described in this report illustrates the analytical performance of DCP and the method development for the analysis of gold milling solutions. Judicious wavelength selections, matrix matching and background techniques have been used to optimize the analytical procedures. Optimal analysis conditions and analyte lines are recommended. Comparative analyses and the results of hydrometallurgical mass balance calculations confirm the usefulness of DC plasma spectroscopy for the determination of precious and other metals in gold milling solutions. Mass balances are generally plus or minus 2 to 5% which is well within potential sampling and testing errors. This is an important consideration in milling operations, where the accuracy of mass balances is of greater interest than the accuracy of the actual analytical data.

Useful analyte lines and their analytical characteristics are summarized herein for their applicability to the analysis of gold-milling solutions.

2.0 LITERATURE REVIEW OF ANALYSIS OF GOLD AND OTHER METALS IN MILLING SOLUTIONS.

2.1 Introduction

The accurate and precise determination of trace level gold and other metals present in milling solutions (pregnants, washes, barren, discharge) and natural waters is required because of economic value and impact on the environment. These analytical determinations provide the data necessary to evaluate the extraction efficiency of the extraction process and the efficiency of gold recovery by traditional zinc precipitation or activated carbon. For complete material balance calculations it is of course necessary to also analyze the head samples and residues. This has become more demanding recently with the interest in processing lower grade ores and difficult ores.

It is necessary to be able to routinely analyze ores and metallurgical products with gold concentrations on the order of 3 grams/ton (3 ppm) and process solutions with gold concentrations of 0.01 mg/litre. It is also necessary to have similar capabilities to confidently determine low levels of other metallurgically and environmentally important metals such as Ag, Cu, Fe, Zn, As and Hg.

Since this report is focussed on the determination of gold and metals in process solutions, the analysis of ores and metallurgical products will not be specifically addressed, although much of the discussion will be applicable.

2.2 Review of Current Analytical Methods

Numerous analytical methods exist for the determination of gold and other metals, but few of these are suitable for rapid, direct, routine analysis of low level concentrations, especially if the samples contain significant concentrations of other metals [1,2]. Current analytical methods for the determination of gold include coulometry, gravimetry, electrogravimetry, polarography, titrimetry, spectrophotometry, fire assay, atomic absorption spectroscopy, X-ray fluorescence, neutron activation analysis and plasma emission spectroscopy. Other metals are generally determined by wet chemical or instrumental methods, particularly atomic absorption and plasma emission spectroscopy.

The classical fire assay methods are generally favoured for the determination of gold, silver and other precious metals in ores and metallurgical products because of the good accuracy and precision attainable. The composition of the resulting precious metal beads is determined either by classical parting and gravimetric methods or spectroscopically after

acid dissolution. Alternative wet chemical extraction and concentration methods have also been developed which have been shown to be effective [3-8]. These methods generally involve aqua regia extraction and pre-concentration by solvent extraction methods using, primarily, methyl isobutyl ketone, diisobutyl ketone and aliquat 336.

Although solutions can also be analyzed by fire assay methods, constant potential coulometry is generally regarded as the referee method for the analysis of gold in solution. However, neither of these methods is particularly well suited for rapid routine analysis due to the extensive sample preparation and manipulation that is required [9,10].

Titrimetric [11,12], gravimetric [11,13] and electro-analytical [14] methods are not commonly used in the analysis of low level gold in process solution because either large samples are required, detection limits are not low enough or serious interferences are encountered due to the presence of other precious metals or high concentrations of other metals present in the matrix. In the case of spectrophotometry, the methods are generally not specific or selective [11, 15]. For these reasons, the analysis of low level gold in process solutions, ores, or metallurgical products by these methods is difficult at best [16].

Instrumental methods, particularly spectroscopy, possess several attractive features for the determination of low level gold and other metals present in process solutions. They are generally more rapid and less expensive for routine analyses and possess or can achieve the required detection limits. Minimal quantities of sample are required and interferences can generally be handled successfully.

The application of X-ray fluorescence spectroscopy (XRF) to the direct analysis of gold milling solutions is somewhat limited by its lack of sensitivity [17]. However, it has been used in the analysis of fire assay beads[18, 19], ion exchange resins [20] and activated carbons from carbon circuits for both precious and base metals [21, 22].

Despite excellent detection limits (0.1 ppb), the use of neutron activation analysis (NAA) has been limited due to the availability of facilities, time required for decay and the chemical separations which are necessary to avoid interference problems. Thus, despite several successful applications [15, 23-26], the usage of NAA for routine analyses is limited.

The most well established, routinely used instrumental method in the metallurgical industry is atomic absorption spectroscopy (AA), although both inductively coupled plasma emission spectroscopy (ICP) and direct current emission spectroscopy (DCP) are gaining wide-spread acceptance as reliable and possibly superior alternatives for the analysis of ores, solutions and products from milling operations.

2.3 Review of Atomic Absorption Spectroscopy and the Analysis of Milling Solutions

Atomic absorption spectroscopy (AAS) is a routine method for the determination of gold and other metals in solution, both in aqueous and some organic solvent media [11]. The method is based on radiation absorbed at resonance wavelengths being proportional to the elemental concentration in solution.

The analysis of gold in solution by AAS is well known and documented in the literature. The useful analytical working range is less than two orders of magnitude, typically from 1 to 20 mg/l [27]. This is not sufficiently sensitive for many process solutions, particularly barren and discharge solutions which contain sub-ppm levels of gold. In addition, calibration curves are frequently not truly linear, requiring second and third order regression treatment to provide accurate data [28].

The determination of gold by AAS is prone to interferences from other elements in solution, particularly iron, copper and calcium, which are often present in milling solutions and tend to suppress results [29-33]. Consequently, the use of releasing agents is routinely required. In addition, mutual interference effect between the noble metals have been observed when determined by flame AAS [34].

The development of solvent extraction preconcentration methods for use with AAS resulted in improved detection limits and elimination of some interference problems [26]. Initially, gold was extracted from acid solutions using methyl-iso-butyl ketone (MIBK) [35]. This was followed by the successful extraction of gold from cyanide solution after oxidation of the Au (I) to Au (III) [36]. The oxidation step was then eliminated by extracting the gold from cyanide solution using n-butyl acetate and trioctylamine [37]. However, the sample had to be acidified. The use of Aliquat 336 and di-iso-butyl ketone (DIBK) allowed the direct extraction of gold from alkaline cyanide solutions into the organic [38]. This solvent extraction preconcentration resulted in a 200 fold improvement in the detection limit of gold. The same extraction system was also applicable to acid media [39].

Thus, the combination of solvent extraction and AAS was a viable analytical method to routinely and rapidly determine low level gold in milling solutions. However, iron, which is an interferent, co-extracted into the organic. Methods have been developed to back-extract the organic phase with dilute acid leaving the gold in the organic phase, free of interference [40, 41].

Advances in AAS have resulted in the availability of flameless atomic absorption spectrometers. This technique has reduced the detection limits of most elements by one or two orders of magnitude. Unfortunately, the determination of gold by flameless AAS suffers serious

interferences from sodium and calcium,both of which are present in milling solutions [42]. This problem can be avoided when flameless AAS is coupled with solvent extraction. Extremely good detection limits have been reported ranging from 0.3 ppb to 4 ppb [8, 43].

The determination of silver and base metals such as Cu, Fe and Zn in milling solutions is required on a routine basis both for metallurgical and environmental reasons. AAS has been used successfully although serial dilutions are necessary in the case of high concentrations. Detection limits are sufficiently low that preconcentration methods are not necessary.

The determination of arsenic and mercury is also required on a routine basis for both metallurgical and environmental reasons. Environmental monitoring is particularly important and analytically demanding. A lack of sensitivity and selectivity and the presence of many interferences and high background causes many difficulties in the direct determination of these elements.

Extraction procedures have been used extensively in the colourimetric determination of small amounts of arsenic and mercury [44].

These include the molybdenum blue and diethyl-dithiocarbamate methods for arsenic and the dithizone and diethyl-dithiocarbamate methods for mercury. Although these methods have high sensitivity, many interferences also exist.

The cold vapour method for mercury [45] is a well accepted sensitive method for the determining of parts per billion of the element. An oxidizing acid attack is used to reduce the mercury in solution to its elemental state. The elemental mercury is then aerated from the solution and the mercury vapour passes through an absorption cell of an AAS. AAS methods for the determination of mercury vary considerably with respect to reagents used and have been described and reviewed [46].

Arsenic in solution is often determined after separation by distillation as the trichloride [47]. However, interferences do exist and the method is not particularly rapid.

The determination of arsenic by hydride generation is a commonly used method and there are many adaptions of the method [48]. The method is rapid, inexpensive and sensitive but prone to interferences from other metals which also tend to form hydrides. Arsenic in solution is converted to arsine in a reducing matrix such as $NaBH_4$ and the arsine swept out of solution by a carrier gas to the spectrometer. Antimony can also be determined from the same solution. Typical detection limits are 1 ppb.

In summary, AAS has been used successfully in the analysis of gold milling solutions. In the cases where the technique does not have the inherent sensitivity required, as in the case of Au, As and Hg in particular, preconcentration and separation methods have been developed. However, with increasing demand for the accurate determinations of several elements, at major, minor and trace levels, simultaneously without the use of preconcentration or separation procedures, AAS may indeed be limited. Atomic emission rather than atomic absorption is inherently more suitable to meet the requirements of selectivity, sensitivity and speed for the determination of multiple elements [49].

2.4 Review of Plasma Emission Spectroscopy and the Analysis of Milling Solutions

A variety of plasma emission spectrometers are commercially available as rapid and reliable instrumental methods for the elemental analysis of a variety of materials [1]. Although many analytical techniques are currently available, plasma spectroscopy alone exhibts a combination of operating characteristics that is unsurpassed by any other single method of analysis. These operating characteristics include excellent precision and accuracy, low limits of detection, wide linear ranges, freedom from chemical and spectral interferences, and multi-element capabilities [50-52].

Various plasma emission sources are available but the most commonly used sources for elemental analyses are the inductively coupled plasma (ICP) and the direct current plasma (DCP). Although these sources differ in how the plasmas are actually generated, the resulting plasmas are fundamentally similar in their properties in an argon atmosphere [51]. The ICP is formed by an electrodeless radio-frequency discharge produced by a magnetically induced current in a flowing argon stream confined to a quartz tube. In contrast, the DCP is produced by a direct current arc discharge formed between electrodes in a flowing argon gas stream.

In both cases, the sample is aspirated and nebulized and the resulting aerosol conducted into the inert argon plasma. The very high temperatures experienced by the sample in the plasma results in the production of excited atoms and ions which emit characteristic radiation which is subsequently focussed, measured and related to elemental concentrations in the original sample.

In the context of this report, the use of DCP has been investigated for its applicability to the analysis of gold milling solutions. For this reason, an extensive discussion of ICP will not be attempted although much of the discussion may be relevant and applicable.

In much of the early literature in the field of plasma emission spectroscopy, DCP was described as being inferior to ICP in its analytical capability. However, much of this was the result of a slower evolution and refinement of the DC plasma emission source which initially had serious stability problems [50, 51]. Another factor limiting its acceptance was its similiarity to conventional arc and spark sources used in spectrographic analysis. Thus, it was not viewed with as much scientific excitement as the ICP was as a new analytical achievement. However, considering the current state of the art in plasma emission analysis, DCP compares very favourably to ICP as an analytical method. [52, 53] Detection limits in general are not as good as those for ICP but are of the same order of magnitude. [53, 54]. In addition,

spectral interferences encountered in DCP spectroscopy appear to be less severe than those reported for ICP-direct reading spectrometer systems [49, 55].

DCP spectroscopy, like ICP, has gained considerable attention as an alternative and comparable method to atomic absorption spectroscopy. [1, 2, 55-60] Potentially, plasma emission spectroscopy is superior to atomic absorption spectroscopy (AAS) due to the inert nature of the argon plasma which eliminates the possibility of re-association of atoms and ions. This reduction in atomic population, which is a serious problem in AAS and limits sensitivity, is completely avoided. [50].

Many applications of plasma emission spectroscopy, too numerous to itemize, are documented in the literature, including the analysis of geologicals, wastewaters and effluents, natural waters, steels, metal scraps, etc. An increasing number of applications are in the field of precious metals analysis of ores and fire assay beads. [2, 16, 28, 34, 61-64]. In contrast, the analysis of precious and other metals in milling solutions, specifically gold milling solutions, by DCP has not been documented in the literature. Although atomic absorption spectroscopy, with or without preconcentration, is the conventional method of routine analysis of solutions from gold milling operations [1], DCP has the potential to be an attractive alternate method based on the

successful usage of DCP in the analysis of saline waters [49, 65-66]. Both saline waters and gold milling solutions contain high levels of sodium and calcium and varying levels of other metals. These alkali matrices present a complex phenomena to plasma emission spectroscopists which must be well understood to ensure reliable analyses.

2.4.1 Review of DC Plasma Source and Characteristics

Plasma emission sources [50], and DC plasma sources in particular [51, 53], have been reviewed in the literature. Unlike flame sources, plasmas are electric discharges and therefore their temperature is not limited by the heat of combustion of a fuel. Considerable quantities of electrical energy can be transferred if the gas is sufficiently ionized and very high temperatures of 6000-10,000^{o} K are attainable.

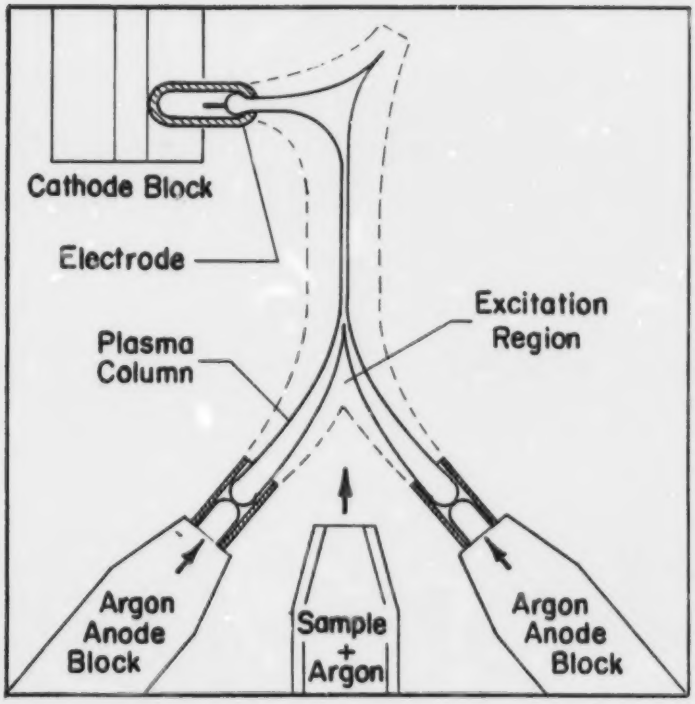
DC plasma sources can be divided into two types. In the first type, analytical observations are made in the current carrying portion of the plasma. In the second type, the analytical observations are made in the flame-like plume or mantle which does not carry the discharge current. It was designed as a primary replacement for flames in spectrometric rather than spectrographic applications.

The first DC plasma sources for spectrometric analysis were developed in 1959 [67, 68] and used two graphite electrodes. This

source suffered severe instability. The stability was subsequently improved by transferring the plasma to an external but integral tungsten cathode [69]. The next major design improvement employed two electrodes inclined at 30° to each other to produce a plasma with a common tail or inverted V configuration [70]. Further minor modification produced a variety of closely related devices. The next major modification employed the same electrode configuration but introduced the sample aerosol from beneath the apex [71]. This reduced the amount of background emission and resulted in better detection limits but serious drifting problems were experienced [72]. This led to the development of a source in which two independent plasma jets shared a single common cathode. The resulting plasma adopted an inverted Y configuration with very good stability, larger excitation zone, reduced interferences and is the source used in the Beckman Spectrametrics DCP emission spectrometers [73]. The Spectrajet is shown schematically in Figure 1.

Considerable research has been performed to determine the properties and characteristics of plasma jets. The plasma in analytical emission spectroscopy cannot attain complete thermal equilibrium since there is always a net transport of energy and mass through the system [51]. This inhomogeneous temperature distribution results in a Local Thermal Equilibrium (LTE). LTE is a desirable state for an analytically useful plasma source because, a) the behaviour of a given element is

FIGURE 1 "Spectrajet" Direct Current Plasma Source



more predictable, b) the kinetic temperature tends to eliminate chemical interferences such as recombination which is common in flame sources and c) instabilities are minimized.

The optimum excitation zone of the plasma is very localized and influenced by the sample. Samples containing alkali or other elements of low ionization potential cause exapnsion of the conducting column of the plasma and weaken the plasma jets from the graphite anodes. The hot plasma expands and causes a disturbance in the gas flows which alters the plasma.

Alkali does not penetrate the plasma deeply but both atom and ion lines experience increases in intensity line-to-background ratio and background. The excitation temperature of the plasma is reduced, especially at the edges where the analytically useful region is located. Thus, the position of maximum intensity is altered due to the change in temperature distribution in the plasma. This effect is manifested as an enhancement of the analyte signal.

Another serious effect is associated with incomplete introduction of the sample aerosol into the plasma [74, 75]. The efficiency of sample introduction is increased by the addition of an easily ionized element such as lithium which allows better penetration into the plasma and normalizes variation in samples.

Background emission of plasma sources is inherently high and limits the detection levels that can be achieved [76, 77]. The high dispersion that is required to obtain good detection limits can be achieved using an echelle grating monochromator. By separating wavelengths and orders, a two-dimensional spectral pattern is produced and the monochromator can be used in the spectrographic as well as spectrometric mode. Such a system is used in the Beckman Spectrametrics DC plasma emission spectrometers.

In summary, the high plasma temperatures that are required for successful DC plasma emission analysis cannot be achieved by a conventional arc or spark source. Stabilized three electrodes arcs are necessary. Although the DC plasma is influenced by the sample and background emission is inherently high, the use of alkali salts to improve sample transport and the echelle grating monochromator to improve background emission ensure that these factors do not limit the analytical usefulness of DC plasma spectroscopy.

2.4.2 Review of the Analytical Performance of DC Plasma Emission Spectroscopy

As previously stated, plasma emission spectroscopy stands alone as the one analytical technique capable of excellent precision and accuracy, low limits of detection, wide linear working range

and reduced spectral and chemical interferences, in addition to multi-element capabilities. Particular advantages of DC plasma emission spectroscopy include long term stability, low power and gas requirements, high versatility with respect to matrices which can be analyzed (aqueous, organic and high salt) and low capital and operating costs.

Emission spectra are inherently rich and there are therefore numerous potential analyte lines from which to choose. Comprehensive listing of spectral lines with appropriate intensity information are invaluable in the selection of useful analyte lines [78]. However, for many elements, the relative intensities exhibited by the spectra excited in plasmas do not correspond exactly to published wavelength tables which are a compilation of data from arc, spark and flame spectroscopy [79]. Once sensitive plasma emission lines are identified criteria such as freedom from spectral interferences, linearity, low stray light contributions and compatability with the working range of the monochromator must be satisfied before an emission line can be considered a useful analyte line.

The desirable analytical properties of DC plasma emission spectroscopy are impressive. Detection limits are low, generally better than those for AAS, comparable to flameless AAS, and on the same order of magnitude as ICP. Precision is very good, generally being 1-2% relative. This type of precision is achieved by minimizing short

and long term drift by using favourable integration times and monitoring standard samples regularly. Accuracy, sensitivity and line to background ratios are also very good. Most impressive though is the wide linear working range, which is generally three to four orders of magnitude. This allows the analysis of a variety of concentration levels, including major, minor, trace and ultratrace, without the need for extensive serial dilutions. This is advantageous both with respect to ease of operation and minimization of systematic errors. Accuracy can be increased if necessary by close bracketing of samples with appropriate standards along various portions of the calibration curve. Close bracketing has also been used in the non-linear portions of calibration curves to further increase the working range [64] but this should be done very cautiously and is probably not advisable. Near the detection limit, continuum and band emissions limit the linearity whereas the upper limit is influenced by the actual operating conditions and physical condition of the electrodes and ceramic sleeves. The freedom from chemical interferences as a result of the high temperatures experienced by samples in the plasma is also advantageous.

Despite these many desirable characteristics, DC plasma has been reported to suffer from spectral interference, high background and matrix effects [56, 57]. These effects however, are not insurmountable and definitely are not limiting.

2.4.2.1 Spectral Interference

The richness of plasma emission spectra provides many potential analyte lines, both atomic and ionic but also can present serious spectral interferences. These interferences, due to stray light, increased continuum emissions, broadened non-analyte lines and direct overlap, can significantly degrade the analytical results. Classical examples of analyses limited by spectral interferences include the determination of boron in steels and trace amounts of hafnium in high zirconium matrices. For successful analyses, severe spectral interferences must be eliminated or reduced through the use of high resolution, high dispersion monochromators such as the Echelle grating monochromator [80 - 82]. The high resolution which can be achieved allows the isolation of the analyte line and also minimizes the effects of broadband background radiation [83].

The echelle grating was originally developed in 1949 [84] and is used in the Beckman Spectrametrics DC plasma emission spectrometers. The echelle monochromator allows for rapid and simple wavelength selection and can be used in the spectrographic or spectrometric modes. When used for short-range scanning (or wavelength profiling), a few spectral bandwidths (± 0.5 mm) on either side of the analyte line can be investigated for spectral interferences.

Based on these scans, a suitable type of background correction can be chosen for use in subsequent quantitative analysis [85]. The alternate method to evaluate the presence of spectral interference is to perform replicate analyses on several analyte lines.

The use of the Echelle grating thus either eliminates or minimizes the great majority of spectral interferences. In the cases where spectral interferences persist with a particular analyte line, other useful analyte lines probably exist in the rich plasma emission spectrum. Consequently, spectral interferences are not limiting in DC plasma spectroscopy.

2.4.2.2 Background Effects

The inherently high background of plasma emission sources is effectively minimized by the use of an Echelle monochromator. Background can also be further minimized by close matrix matching, corrections or extraction of the analyte from the sample matrix.

The analytically useful region of the DC plasma source is a very localized excitation zone. [56, 57]. Within this optimum excitation zone, background emission is low and constant resulting in a very favourable line to background ratio. Although the excitation zone is generally 5.0 to 5.2 mm above the anode sleeves [65], its

exact position is different for every analyte line. The optimal position must be determine by vertically profiling the emission intensity and background to ensure the best possible sensitivity. The optimal position in the excitation zone varies from very low in the plasma for refractory metals, to quite high in the plasma for easily ionized metals. The optimal position for analysis in the excitation zone is also influenced by the gas flows and physical condition of the electrodes and should always be optimized.

Through the use of close matrix matching, variations in background can be accounted for and compensated. This particularly important in the case of high salt matrices, but not nearly as critical in acid matrices.[34]. In the case of severe background, corrections can be used to eliminate or minimize the effect.[85]. The size of the entrance and exit slits in the echelle monochromator can also be reduced to minimize background. However, this may result in some loss in sensitivity.

The use of solvent extraction procedures is a common analytical method to reduce the effects of interferences and background due to a sample matrix. The extraction of gold using MIBK is one of the most common solvent extraction methods in atomic spectroscopy. It has been used successfully in conjunction with atomic absorption spectroscopy, as described in a previous section. Its usefulness

however in conjunction with plasma spectroscopy may be limited.[62]. Many organic solvents commonly used exhibit strong molecular band emissions which contribute to background. In addition, dissolved water entrained in the organic phase can contribute strong hydroxyl emission bands. Background emission due to organic solvents appears to influence ion lines more than neutral lines. Therefore, it may be possible to effectively use solvent extraction methods in conjunction with plasma spectroscopy by choosing the more intense neutral rather than ion analyte lines. [87]. Precise wavelength and vertical profiling, and improved nebulization of the organic and transport of aerosol could also improve analytical results. Consequently, better detection limits may be attainable by plasma spectroscopy as a result of enhancing the analyte intensity relative to the background in organic matrices.

In summary, background effects do not limit the usefulness of DC plasma spectroscopy in aqueous, high salt and organic matrices. The use of matrix matching, background corrections and solvent extraction can all be used effectively to improve analytical performance.

2.4.2.3 Matrix Effects

As previously stated, DC plasma spectroscopy has been said to suffer from matrix effects. This complex phenomena must be well understood as it can be either detrimental, manageable or potentially useful. [49, 50, 52, 53, 55, 56, 60, 65, 66, 89, 90].

Matrix and interferent matching of samples and standards is desirable to minimize effects the matrix and major interferences may have. This need not be a long and tedious process since major effects are due to high concentrations of easily ionized elements such as alkalis and alkaline earths. which influence nebulization, aerosol transport and excitation properties of the source.

High concentration of alkali, particularly sodium, can be detrimental because the position of maximum intensity in the highly localized zone is altered. If this is unaccounted for during the analytical determinations, serious enhancement effects will occur.

The alkali effect is complex [60, 65]. The effective temperature of the plasma core is decreased and the excitation zone is expanded. This allows better volatilization of the sample and deeper penetration into the plasma. Consequently, the effective temperature experienced by the analyte is increased as it rises in the

expanded plasma core and signal enhancement is observed.

The amount of enhancement observed decreases as the ionization potential of the metals decrease. However, it is observed for both atom and ion lines which strongly suggests that the effect cannot be due to suppression of ionization. Therefore, deeper penetration of the analyte into the plasma is the probable mechanism responsible for the alkali effect.

Since the alkali effect can vary considerably from sample to sample, standardization of the effect is desirable to reduce the matrix effects. The use of buffering by an easily ionized salt such as lithium nitrate results in a constant alkali level and constant background emission level in the optimal viewing zone of the plasma source. Consequently, the enhanced analyte intensity can be measured relative to a low and constant background to yield improved sensitivity and lower detection limits. This however, is only possible if matrix matching is performed. Without matrix matching falsely high determinations would result.

The greatest enhancement has been observed with ionic lines of transition metals with unfilled d-subshells, especially if the d-electrons are unpaired. In contrast, atomic lines show greater enhancement if the d-subshells are filled. [60]. This experimental observation helps explain why the detection of low level gold in milling

solutions is favourable by DCP using the atomic emission lines at 242.8 and 276.6 mm. The gold is present in solution as $Au(CN)_2^-$ which has a d^{10} configuration and therefore subject to significant enhancement and improved sensitivity providing that close matrix matching is employed.

The other major matrix effect is due to the presence of alkaline earths in solution. Calcium in particular, and magnesium to a lesser extent, can be responsible for stray light problems if present in appreciable levels. Stray light interferences are the result of near scatter and reflections which occur in the secondary optics and these can contribute to the intensity of other analyte lines. This results in elevated background and higher detection limits. The effects are most severe when the analyte emission and calcium emission are of the same order. The actual severity and magnitude of the interference depends on the relative intensities of the analyte and calcium emission lines. Very strong analyte lines will be influenced less than weak analyte lines by stray light.

Stray light effects are greatly reduced by the echelle monochromator, matrix matching and background corrections if applicable. If stray light problems do persist, another analyte line, which will be less influenced by stray light, can be chosen since emissions spectra are so rich. These considerations are of importance in the analysis of

gold milling solutions because lime is added to leaching circuits to maintain an optional alkalinity level to ensure good extraction.

In summary, if the alkali and stray light effects are kept in mind, and close matrix matching is employed, DC plasma spectroscopy is not limited. In fact, the matrix effects that were initially considered detrimental can be favourable in some cases.

2.4.2.4 Multi-Element Capability

Extensive efforts to develop and validate analytical methods for the determination of several elements simultaneously while avoiding the need for preconcentration, dilution and/or separation procedures have been reviewed. [49]. Atomic emission spectroscopy has the desireable features consistent with the analytical requirements. Both ICP[49] and DC plasma [52, 55, 57] spectroscopy have been shown to be capable of multi-element analysis. In the case of DC plasma spectroscopy, fast sequential multi-element analysis is available in addition to simultaneous multi-element analysis. [88].

The advantages of increased sample throughput and reduced costs per analysis are obvious with multi-element analysis. However, it must be stressed that multi-element analysis is necessarily a compromise situation. Optimal operating conditions

cannot be realized for a large suite of elements simultaneously. [16]. In particular, vertical profiling for each analyte line and individual background corrections are not possible as they are in the sequential mode. Consequently, it is necessary to carefully choose a suite of elements that can be successfully determined simultaneously with minimal losses in accuracy and minimal error. For example, it is not recommended that alkali and refractory metals be determined simultaneously since they have significantly different optimal positions in the excitation zone of the DC plasma source.

Another serious consideration is potential inter-element and matrix effects which may go undetected while voluminous analytical data is generated. The use of certified standard samples and/or internal standards is imperative to monitor the validity of all data. This should be standard practice. Common sense should not be less respected than the tremendous potential of multi-element analysis.

A third consideration is the need to resist attempts to use a single method which may be an unjustified and undesirable compromise to produce a single solution for multi-element analysis. For example, in the case of precious metal ores, the precious metals themselves are probably best determined following fire assay methods whereas base metals can be determined following acid dissolution.

In the case of gold milling solutions, multi-element analysis can be successfully used to determine gold, silver and base metals, providing that compatible wavelengths are chosen. Environmentally important arsenic and mercury determinations are probably best performed sequentially.

2.4.3 Summary of Analytical Performance of DC Plasma Emission Spectroscopy

DC plasma spectroscopy is very well suited to the analysis of gold milling solutions due to its high accuracy and precision, low detection limits, wide linear working range, freedom from interferences and multi-element capability. Additional advantages include long term stability, low power and gas consumption, high versatility, and low capital and operating costs.

The capability to determine low levels of gold in milling solutions, directly, without the need for preconcentration is a major advantage of DC plasma over atomic absorption spectroscopy. The high temperature of the plasma source ensures that chemical interferences are rarely encountered. In addition, re-association of atoms and ions in the plasma does not occur. Thus, the sensitivity for precious metals is equal or better than that for atomic absorption. High resolution capabilities eliminate or minimize spectral interferences between precious metals and other metals.

The use of argon gas eliminates any reducing atmosphere in the spray chamber. Therefore potential contaminants or precious metals themselves do not deposit or accumulate.

Despite these numerous and significant advantages plasma spectroscopy should not be considered as an "ultimate" analytical technique. There are inherent phenomena that are potentially problematic. The richness of emission spectra and the small, highly localized excitation zone necessitate the use of the high resolution, high dispersion echelle monochromator to eliminate or minimize spectral interferences, background and plasma sensitivity. Changing source properties when high alkali concentrations are present must be well understood and compensated for by close matrix matching to ensure reliable data.

The tungsten and graphite electrodes used to form the DC plasma produce their own spectral emission. In contrast, ICP which uses an electrodeless discharge, does not exhibit this spectral contamination.

In summary, although potential difficulties do exist, the use of DC plasma spectroscopy is not limited providing that these effects are recognized and properly addressed. The advantages of

plasma spectroscopy outweigh the disadvantages. It has been shown to be an effective instrumental method of analysis which is comparable to and in some respects superior to atomic absorption and ICP spectroscopy.

3.0 EXPERIMENTAL

3.1 Instrumentation

Beckman (Spectrametrics) Spectraspan ^{R} Direct Current Argon Plasma Emission spectrometers with three electrode plasma jets were used in this testwork [80, 81, 86]. The majority of the testwork was performed using the Spectraspan IIIB multichannel model in the sequential mode. This echelle grating direct reading spectrometer is equipped with micro-processor based control and data acquisition system, background corrector and photographic attachment. Analyses were also performed on the Spectraspan IV which is a single channel spectrometer with no background corrector or photographic attachment. A Spectraspan VI, which is a computer controlled, fast seqential multichannel spectrometer was also used.

These spectrometers differ from other commercially available spectrometers both with respect to their source and optics. The source is a stable high energy DC argon plasma formed between a tungsten cathode and two carbon anodes and has an inverted "Y" configuration. The optical design is a modified Czerny-Turner system using an echelle grating with 30° prism for order separation. The optical specifications of this monochromator are listed in Table 1.

TABLE 1 OPTICAL SPECIFICATIONS OF SPECTRASPAN III B

Wavelength Range	190 to 800 nm
Spectral Orders	28th to 118th
Focal Length	75 cm
F number	f/13
Grating Width	9.6 cm
Grating Height	4.6 cm
Diffraction Angle	63° 26'
Grating Spacing	79 grooves/mm
Dispersion	6.1 nm/mm at 200 nm
	12.2 nm/mm at 400 nm
	24.4 nm/mm at 800 nm
Spectral Bandpass	.15 nm at 200 nm
	.30 nm at 400 nm
	.60 nm at 800 nm

The resulting two dimensional spectral pattern can be used in the spectrographic mode for qualitative identification or in the monochromatic (photoelectric) mode for quantitative analysis.

Emission from the source is focussed through an adjustable exit slit followed by a Hammamatsu R292 photo-multiplier. The input slits are adjustable from 25 x 100 nm and the output slits from 25 x 100 nm to 200 x 200 nm.

The spectrometer is operated at 40V and 20 Amps using prepurified argon as the carrier gas. Sample solution is perstaltically pumped at a rate of 2 ml/minute, pneumatically neubulized and aspirated into the plasma. Waste solution is pumped from the sample chamber.

Background correction and spectral profiling of analytical wavelengths is possible using a hardware and software package supplied as a spectrometer component described as DBC-33 [85]. A few spectral bandwidths on either side of the analyte line can be investigated for suspected spectral interferences. Various background corrections are available by measuring off peak intensities.

3.2 Operating Conditions and Procedures

Although commercial grade argon (99.5%) is reportedly satisfactory, the spectrometer was operated using pre-purified argon (99.998%) at a rate of 7 l/min. The optimal argon pressure at the nebulizer is on the order of 24 psi and 50 psi at the sleeves, but varies from spectrometer to spectrometer. The argon pressure is divided equally among the cathode and two anodes. Fine adjustments of the argon flow are made to optimize the plasma. The approximate excitation temperature of the plasma is 6000 to 7000°K.

Entrance slits to the echelle monochromator are normally 50 x 300 nmand exit slits 100 x 300 nm. These selections generally provide the best combination of sensitivity and limited noise and background radiation.

Wavelength selection and scanning is accomplished using the spectrographic (diagnostic) mode of the echelle. The order of the analyte line is selected and then the specific wavelength within that order is finely tuned to maximize the signal intensity. Background emission and noise are minimized by vertically profiling the plasma emission by adjusting the vertical position of the plasma source relative to the monochromator entrance slit. For all vertical positions,

the entrance was horizontally equidistant from the pair of anodes. The optimal viewing position is a very small zone approximately 5.0 to 5.2 mm above the ceramic sleeves. The actual position is dependent upon the element in question.

Quantitative analyses are performed in the photoelectric (integration) mode. The photomultiplier is set as low as possible to reduce dark current noise and the gain is then automatically set by the microprocessor control. The upper limit of the calibration range is set with a high standard and the lower limit set with a low standard or blank. Using this two point calibration the microprocessor is used to convert emission intensity to concentration by linear interpolation. Extrapolation beyond the high standard is also possible, but caution must be exercised not to exceed the linear working range. Generally, three five second integrations are performed for routine analysis. Longer integration periods are advisable when low analyte concentrations must be determined.

All reagents used are of high purity.

4.0 DC PLASMA ANALYSIS OF MILLING SOLUTIONS

To determine the applicability of DC plasma analysis to gold milling solutions, analyte lines were selected for gold, silver, copper, iron, zinc, mercury and arsenic. The properties of the lines in a high sodium and calcium matrix were determined in order to provide the information required to judiciously select the lines which will perform well in the analysis of gold milling solutions.

Several gold ores, typical of various Canadian deposits were leached. The solutions resulting from the leach were analyzed by various techniques using DC plasma emission analysis. Recommendations were made to enable accurate analysis by DC plasma.

4.1 Evaluation of Potential Analyte Lines

By evaluating the analytical characteristics and interferences of several intense emissions lines, lines for analytical determinations were selected. Table 2 lists the analyte lines investigated. The lines were chosen on the basis of their common usage in atomic absorption and emission spectroscopy.

TABLE 2 Potential Analyte Lines

Element	Wavelength (nm)	Element	Wavelength (nm)
Au	242.795 (242.8)	Fe	238.204 (238.2)
	267.595 (267.6)		259.940 (259.9)
	312.275 (312.3)		371.994 (372.0)
Ag	328.068 (328.1)	Zn	202.548 (202.5)
	338.289 (338.3)		206.200 (206.2)
	546.549 (546.6)		213.856 (213.9)
Cu	213.598 (213.6)	As	193.696 (193.7)
	224.700 (224.7)		228.812 (228.8)
	324.754 (324.8)		
	327.396 (327.4)	Hg	253.652 (253.7)
	521.820 (521.8)		546.074 (546.1)

4.1.1 Line Characteristics

Each line was investigated by determining the detection limit, linear dynamic range (LDR), background equivalent concentration and precision in a cyanide matrix. The definitions of these characteristics were obtained from the Handbook of Spectral Line Characteristics for the DC Plasma/Echelle Systems. In this way, the effect of a cyanide matrix may be seen at a glance by comparing the Handbook values to the corresponding cyanide matrix values. The definitions of these characteristics follow:

Detection Limit

The analyte concentration corresponding to a signal which is equivalent to three times the background noise standard deviation at the analyte line. The signal was integrated over a 10 second period for 9 consecutive measurements.

Linear Dynamic Range (LDR)

The low end of the range was defined to be equal to ten times the detection limit. The high end was defined as the highest concentration to which the standard curve was within 10% of perfect linearty.

Background Equivalent Concentration (BEC)

The analyte concentration which is equivalent to the signal generated by the plasma and matrix at the analyte line.

Precision

The relative deviation on a set of nine 10 second measurements.

The high end of the LDR was determined by the following procedure: The spectrometer was calibrated with 100 ppm of metal in a cyanide matrix as the high standard and the cyanide matrix as the blank. Standards prepared in the cyanide matrix containing 80, 50, 40, 20, 10 and 1 ppm were assayed. If the results were not within 10% of perfect linearity, the spectrometer was recalibrated with successively lower standards until acceptable linearity was obtained. If the results were within 10% of perfect linearity, the spectrometer was calibrated with successively higher standards until the concentration at which the linearity broke down was determined.

The detection limit, precision and BEC were determined by calibrating the spectrometer with a high standard which was estimated to be approximately 10 times the BEC and the cyanide matrix as the blank. The matrix solution was aspirated and nine consecutive 10 second integration counts were recorded. The high standard was then aspirated and 9 consecutive 10 second integrated counts were recorded. The following calculations were then performed using the data generated.

$$\text{Counts per ppm} = \frac{\bar{x} - \bar{y}}{[HS]}$$

$$DL = \frac{3\sigma_y}{\text{counts per ppm}}$$

$$BEC = \frac{\bar{y}}{\text{counts per ppm}}$$

$$\% \text{ Precision} = \frac{\sigma_x}{\bar{x}}$$

where x = high standard counts

y = blank matrix counts

[HS] = concentration of high standard in ppm

Appendix I contains the data sheets for each of the lines investigated. The data sheets contain the order of the wavelength and the state of emission as well as the analytical characteristics.

4.1.2 Interferences

The interferences on each line were determined by aspirating 1000 ppm of the interferent and measuring the intensity of the resulting signal. The spectrometer was calibrated with 10 ppm of the analyte and deionized water as the blank. Two five second integrations of the signal generated by the interferent were recorded. The results are thereby reported as analyte ppm due to 1000 ppm of the interferent. The linearity of the interferent effect was not investigated. It must be kept in mind that these results are only meaningful in the identification of interferents and their intensities in relation to each other.

Table 3 lists the elements tested for interference on the lines investigated and the resulting analyte ppm if a reading of greater than 0.05 ppm was obtained.

TABLE 3 Interferences on Investigated Analyte Lines

	Au 242.8	Au 267.6	Au 312.3	Fe 238.2	Fe 259.9	Fe 372.0	Hg 253.6
Al	--	--	--	0.1	--	0.08	2.0
Sb	--	--	--	0.07	--	--	--
As	--	--	--	--	--	--	--
Ba	--	--	--	0.1	--	--	
Bi			0.2	--	0.04	0.07	--
Cd				0.06	--	--	--
Ca	--	--	--	--	--	--	--
Cr	--	0.3	1.8	0.1	--	0.1	--
Co	0.05	0.6	0.3	0.4	0.07	0.06	20.0
Cu	--	--	--	0.08	--	0.1	--
Au	--	--	--	0.6	0.5	0.6	--
In			--	--	--	--	--
Fe	0.05	0.02	1.1	--	--	--	0.5
Pb	--	--	--	0.2	0.1	0.2	--
Mn	1.9	--	--	--	0.6	--	--
Mg	--	--	--	0.1	0.4	--	--
Hg	--	--	--	--	--	--	--
Mo	--	--	1.0	--	--	0.7	
Ni	--	--	--	0.5	0.3	0.5	--
Nb			2.5	--	0.3	0.7	
Pd	--	--	--	--	--	--	--
Pt	0.4	--	--	1.3	--	--	5.0
K			--	0.2	--	--	--
Re	--	0.07	--	0.5	0.06	0.07	0.1
Ag	--	--	--	--	--	--	--
Na	--	--	--	--	--	--	0.2
Th	5.7	0.07	3.0	--	--	--	
Ti	0.2	--	5.4	1.1	1.0	1.7	--
U	0.1	0.8	5.0	0.14	0.5	1.5	--
V	--	0.2	26.7	0.7	0.7	0.5	--
Zn	--	--	--	0.07	--	--	--

TABLE 3 Interferences on Investigated Analyte Lines cont.

	As 193.7	As 228.8	Cu 213.6	Cu 224.7	Cu 324.8	Cu 327.4	Cu 521.8
Al	0.2	--	--	--	--	--	1.0
Sb	0.09	--	--	--	--	--	--
As	--	--	--	--	--	--	--
Ba	--	--		--	--	--	1.0
Bi	--	--	--	--	--	--	--
Cd	--	>20		--	--	--	--
Ca	0.07	--	--	--	--	--	0.4
Cr	0.09	--	--		--	--	1.6
Co	--	1.1	--	--	--	--	0.2
Cu	--	--	--	--	--	--	--
Au	--	--	--	--	--	0.08	--
In			--	--	0.1	--	--
Fe	0.1	--	0.13	--	--	--	0.2
Pb				0.3	--	--	--
Mg	0.08	--	--	--	--	--	0.05
Mn	--	--	--	--	--	--	0.3
Hg	--	--	--	--	--	--	0.1
Mo	--	--		--	0.3	--	2.0
Ni	--	1.1	--	--	--	--	0.2
Nb	--	--	--	--	1.5	.3	3.7
Pd	0.09	--	--	--	--	--	--
Pt	1.3	9.8	--	0.1	--	--	--
K	--	--	--		--	.05	--
Re	--	--		--	--	--	0.4
Ag	--	--	--	--	--	--	--
Na	--	--	--	--	--	--	--
Th	0.1	0.2	--	--	.3	2.9	2.8
Ti	0.1	0.2		0.2	.1	0.3	16.1
U	--	0.4	--	0.05	.3	0.7	5.7
V	1.0	1.2	--	--		0.1	5.2
Zn	--	--	0.07		--	--	--

-- : interference less than 0.05 ppm of analyte

TABLE 3 Interferences on Investigated Analyte Lines cont.

	Ag 328.1	Ag 338.3	Ag 546.6	Zn 202.5	Zn 206.2	Zn 213.9
Al	--	--	0.8	--	--	--
Sb	--	--	--	--	--	--
As	--	--	--	--	--	--
Ba	--	--	1.8	--	--	--
Bi	--	0.4		--	--	--
Cd	--	--	--	--	--	--
Ca	--	--	6.6	--	--	--
Cr	--	--	--	0.08	--	.07
Co	--	--	--	--	--	--
Cu	0.1	--	--	--	--	--
Au	--	--	--	--	--	--
In	0.4	.4	--	--	--	--
Fe	--	--	--	--	--	.07
Pb	--	.05	--	--	0.1	--
Mg	--	--	--	--	--	--
Mn	0.05	--	--	--	--	--
Hg		.06	--	--	--	--
Mo	0.5	.08	20	--	--	--
Hg	--	--	--	--	--	2.6
Nb	0.08	.3	13	--	--	--
Pd	--	.02	--	--	--	--
Pt	--	--	--	--	--	--
K	--	--	--	--	--	
Re	--	--	1.0	--	--	--
Ag	--	--	--	--	--	--
Na	--	--	--	--	--	--
Th	0.5	0.7	5.0	--	--	--
Ti	0.4	1.4	50.	--	--	--
U	0.8	1.2	40	--	--	--
V	0.2	.1	.11	--	--	--
Zn	--	--	--	--	--	--

--: interference less than 0.05 ppm of analyte

4.1.3 Line Selection

4.1.3.1 Gold Lines

Gold spectral emissions at 242.8 , 267.6 and 312.3 nm were chosen on the basis of their extensive usage in analysis.

Gold emissions at 197.8, 208.2 and 211.1 nm are potentially useful lines. However, their intensities are low and this reduces their sensitivity to low level gold solutions. Investigations of these lines were not pursued.

Table 4 summarizes the characteristics of the three investigated lines. The characteristics determined by Spectrametrics with an acid solution are included in the Table for comparison.

TABLE 4

Summary of Au Line Characteristics

Line nm	Major Interference	Analyte ppm	Linearity	Limit of Det^{n}	BEC	Precision
Au 242.8	Th	5.7	0.3-100ppm	0.03	1	0.76
	Mn	1.9				
Acid Matrix			0.8-100	0.008	0.3	0.9
Au 267.6	Co	0.6	0.2-100ppm	0.02	2	0.64
	U	0.8				
Acid Matrix			0.8-100	0.008	0.2	1.0
Au 312.3	Fe	1.1	3-100 ppm	0.3	4	0.27
	Mo	1.0				
	U	5.0				
	Th	3.0				
	Ti	5.4				
	V	26.7				
	Cr	1.8				
	Nb	2.5				
Acid Matrix			0.4-1000ppm	0.04	2	0.7

The cyanide matrix had least effect on Au 242.8 nm. The limit of detection was increased by a factor of 2.75 thereby raising the lower end of the linear dynamic range. However, linearity was retained to 100 ppm. The BEC was increased by a factor of three while the precision was improved by almost 20%.

Reduction of the LDR occurred at Au 267.6 nm, with the low end of the range rising from 0.08 to 0.2 ppm. A BEC ten-fold higher than that of an acid matrix was observed. The limit of detection was raised by a factor of 2.5. Again, the precision was improved, this time by over 50%.

Au 312.3 nm displayed the greatest variations in its characteristics between acid and cyanide matrices. The LDR fell from 4 orders of magnitude to 2. The lower end of the LDR was raised to 3 ppm which severely hampers the use of this line in analysis of gold milling solutions. The limit of detection increased to 0.3 ppm and the BEC doubled. Interestingly, the greatest improvement in precision of the three lines occurred (160%). It is obvious that this line is extremely matrix sensitive. The stray light from the calcium greatly increased the limit of detection. On the other hand, the ionization buffering effect of the sodium results in very good precision.

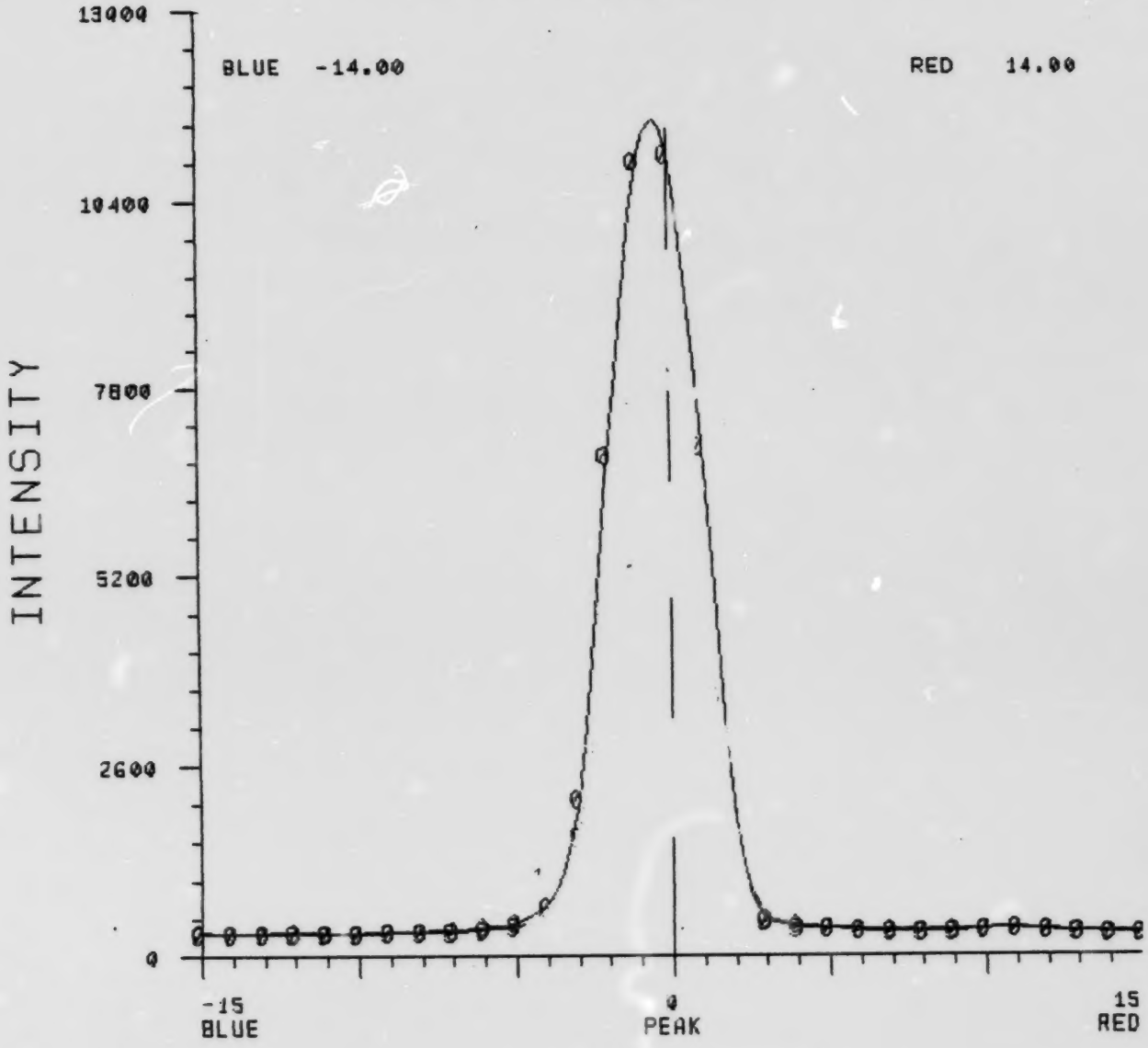
Au 242.8 nm has significant interferences from thorium and manganese when these elements are present in high levels. Au 267.6 nm has the least interferences with small contributions to the signal by cobalt and uranium. Many elements interfere with Au 312.3 nm including significant contributions by the commonly co-occurring elements Fe, Mo, V, Cr.

Based on the line statistics and interferences, it is recommended that Au 312.3 not be used for gold analysis in a cyanide matrix. The large LDR of this line in acid solution constituted an advantage over the other two lines. However, the cyanide matrix eliminates this advantage resulting in Au 242.8 nm and Au 267.6 nm possessing the best LDR. The high limit of detection and the large number of interferents justifies the abandonment of this line.

The spectral emissions at 242.8 nm and 267.6 nm have comparative characteristics and no advantage for either can be seen on this basis. Figures 2 and 3 contain the wavelength profiles for Au 242.8 nm and Au 267.6 nm respectively. The profiles were obtained using a solution containing a high level of gold as well as high levels of copper, iron, sodium and calcium. A clean gold peak is observed at both analyte lines.

FIGURE 2

Au 242.8 nm Wavelength Profile

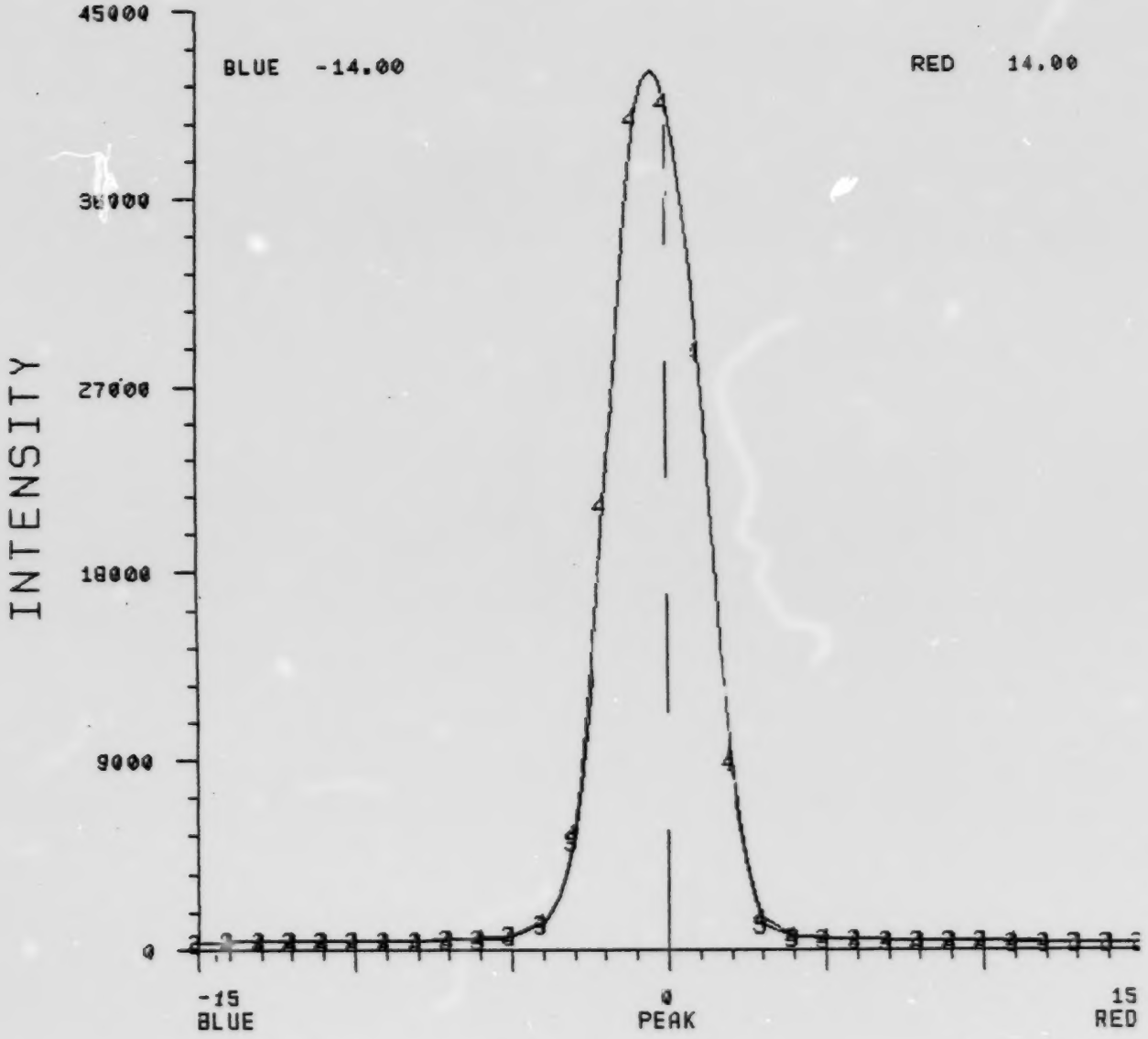


Matrix Composition

Cu	1000 ppm	Ag	20 ppm
Fe	500 ppm	Na	3300 ppm
Zn	10 ppm	Ca	1000 ppm
Au	120 ppm		

FIGURE 3

Au 267.6 nm Wavelength Profile



0.0024 nm/step

Matrix Composition

Cu	1000 ppm	Ag	20 ppm
Fe	500 ppm	Na	3300 ppm
Zn	10 ppm	Ca	1000 ppm
Au	120 ppm		

The ability of the DCP to assay sub ppm levels of gold in a cyanide matrix is shown in Figures 4 and 5. Process solutions containing 0.01 to 0.5 ppm were also scanned at 242.8 nm and 267.6 nm respectively. With suitably matched standards, the background contribution to the analyses is eliminated allowing accurate determinations of low levels of gold.

4.1.3.2 Silver Lines

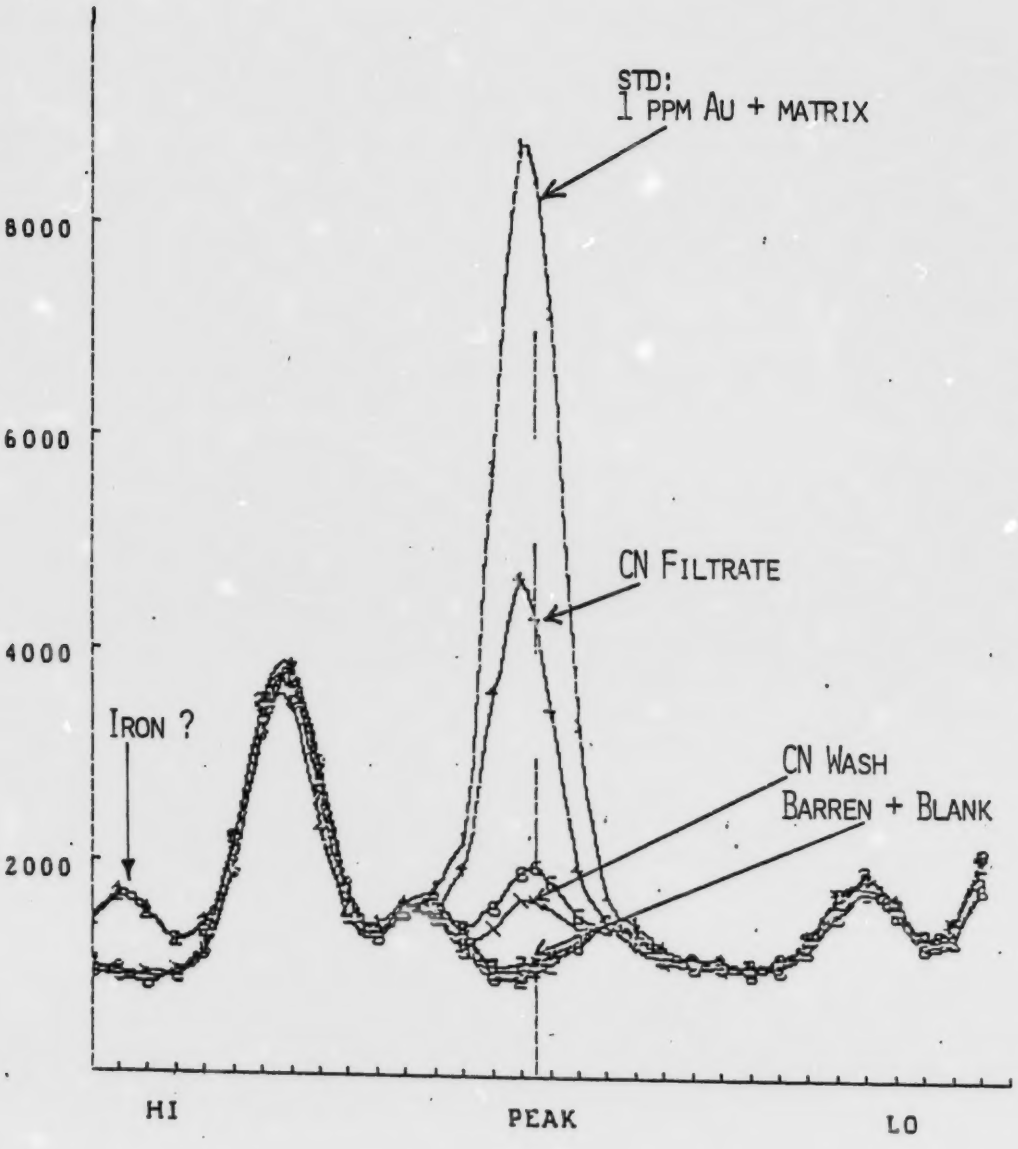
The detection limit of the silver emission at 328.1 nm was raised from 0.004 ppm in an acid matrix to 0.01 ppm in a cyanide matrix. The BEC increased by a factor of 6 to 0.6 ppm. The LDR is reduced by the cyanide matrix to 0.1 - 2.5 ppm. The precision of the line was found to be 0.26%.

The cyanide matrix had least effect on the emission at 338.3 nm. The LDR narrowed slightly to 0.2 - 80 ppm. The limit of detection rose to 0.02 ppm and the BEC increased to 0.5 ppm. The precision of this line remained comparable to acid matrix.

The emission at 546.6 nm remained comparable to the acid matrix for the limit of detection, BEC and precision. The linear dynamic range however decreased to 1-300 ppm compared to the high end of 1000 ppm for acid matrices.

FIGURE 4

Au 242.8 nm - Scans of Low Level Gold Process Solutions



.0009 nm/step

FIGURE 5

Au 267.6 nm - Scans of Low Level Gold Process Solutions

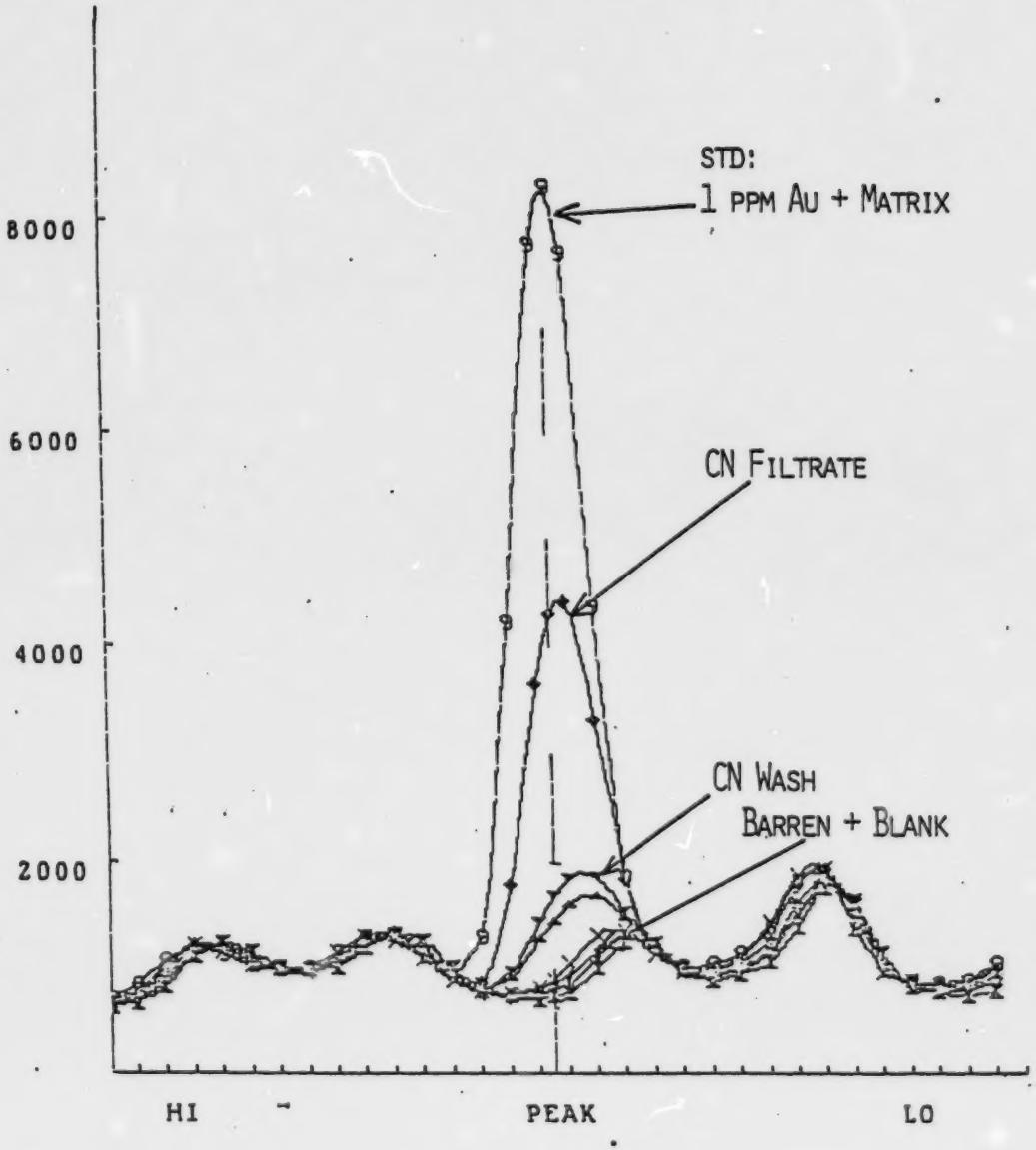
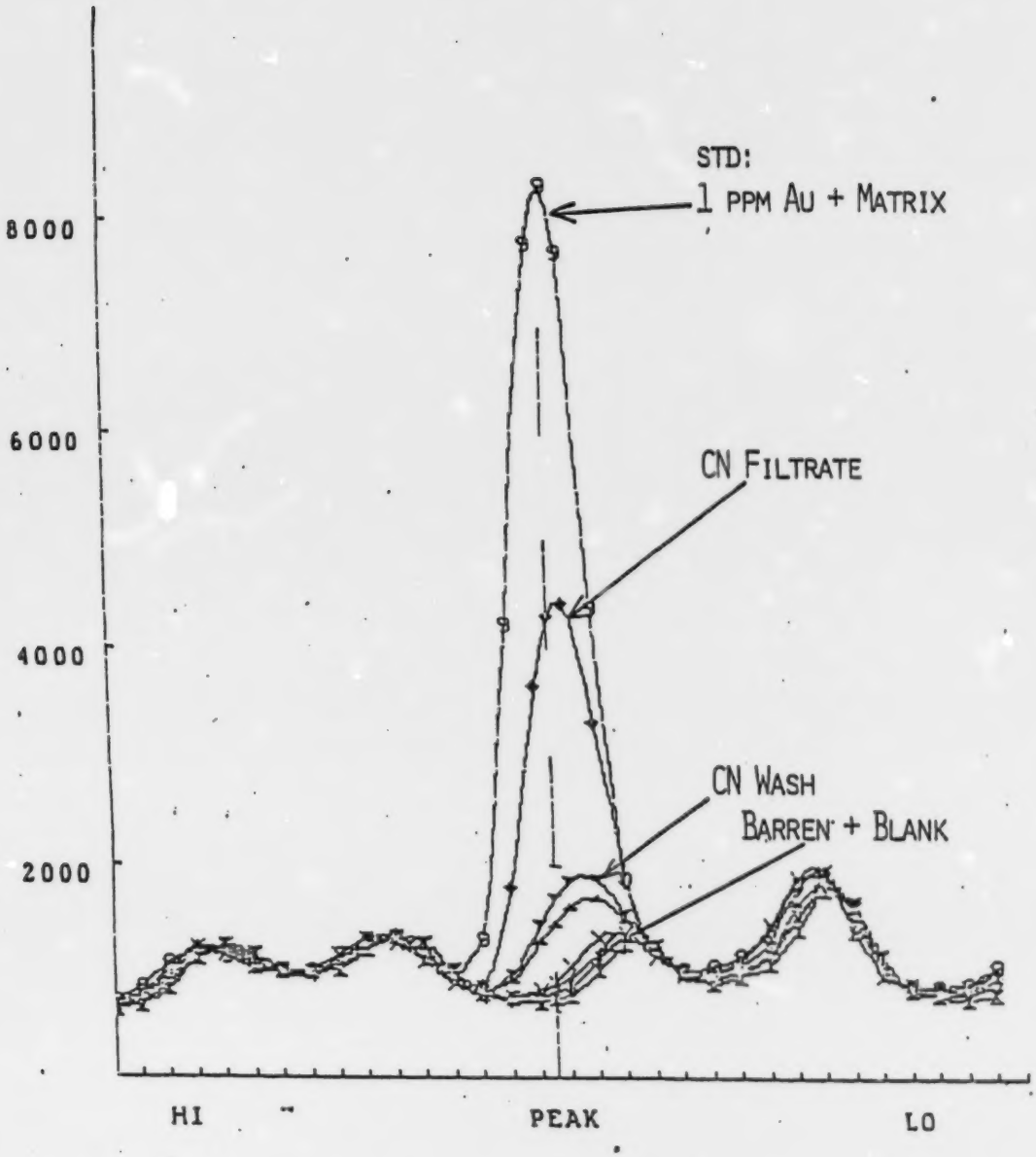


FIGURE 5

Au 267.6 nm - Scans of Low Level Gold Process Solutions



Small interferences from uranium and thorium are present at 328.1 nm. At 338.3 nm, uranium and titanium interfere slightly. A large number of strong interferents effect the emission at 546.5 nm. Most notable of them are calcium, molybdenum, uranium and titanium. The calcium interference is of great concern since gold milling solutions invariably contain high levels of calcium due to the lime additions required for alkalinity control. The molybdenum and titanium interferences are also of concern since these metals often occur in gold ores.

The lines 328.1 nm and 338.3 nm are both recommended for analysis. If a solution of greater than 20 ppm Ag was to be determined, the emission at 338.3 nm would be recommended since it has a larger LDR than that at 328 nm. Table 5 summarizes the characteristics of the silver lines investigated.

Figure 6 illustrates the wavelength profile at 328.1 nm. The solution contained 20 ppm silver in the matrix for leach No. 2. This matrix contains high Cu, Fe, Ca, Na and Au. As can be seen, there is a clean background with no spectral interferences from the elements investigated.

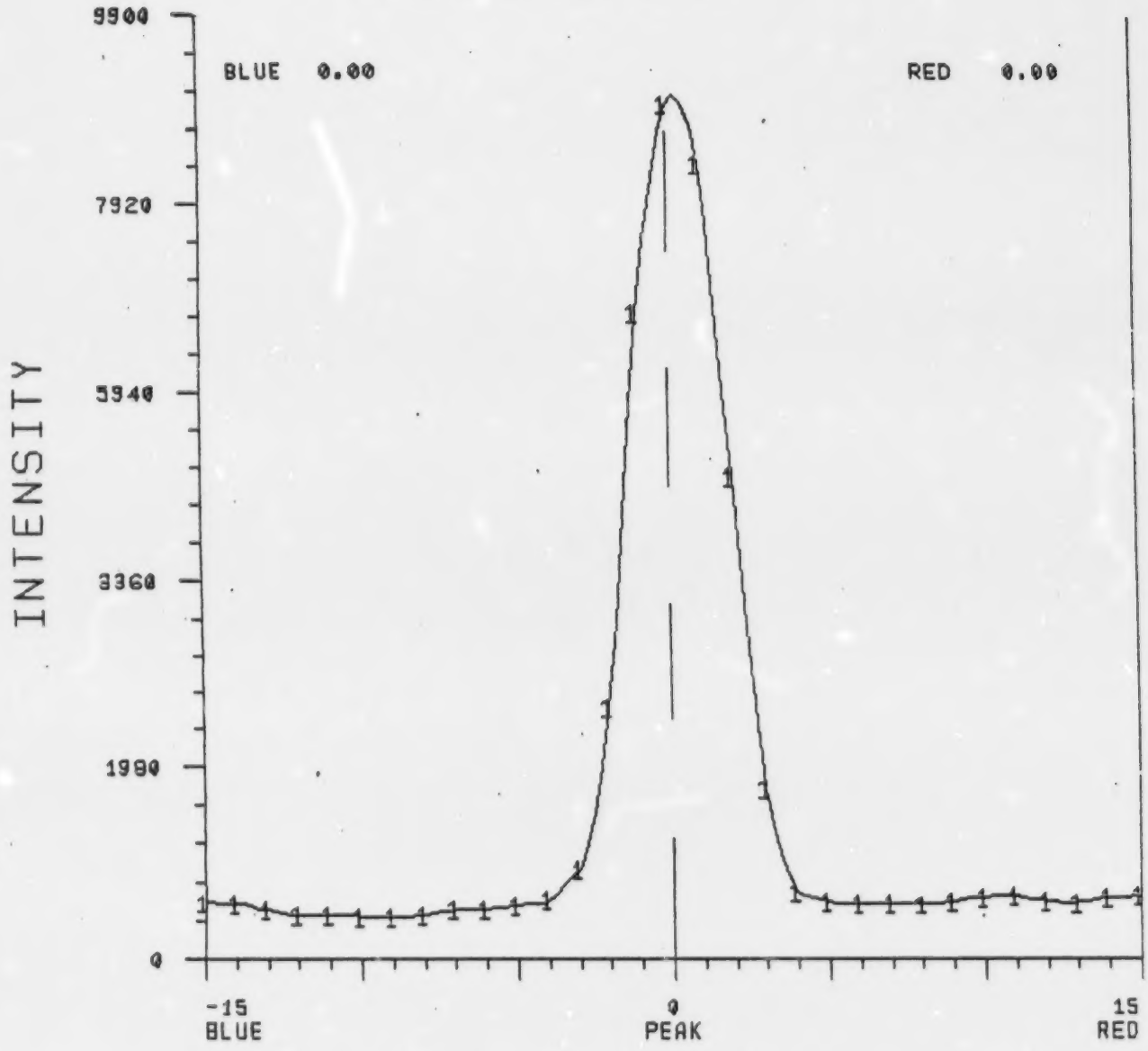
TABLE 5

Summary of Ag Line Characteristics

Line nm	Major Interferent	Analyte ppm	Linearity	Limit of Det^{n}	BEC	Precision
328.1	U	0.8	.1-25	0.01	.6	.26
	Th	0.5				
338.3	U	1.2	.2-80	0.02	.5	.58
	Ti	1.4				
546.5	Ca	6.6	1 - 300	0.1	4	.52
	Mo	20.0				
	Ba	1.8				
	Re	1.0				
	U	40.0				
	Th	5.0				
	Ti	50.				
	V	11				
	Cr	2.7				
	Nb	13.3				

FIGURE 6

Ag 328.1 Wavelength Profile



0.0029 nm/step

Matrix Composition

Cu	1000 ppm	Ag	20 ppm
Fe	500 ppm	Na	3300 ppm
Zn	10 ppm	Ca	1000 ppm
Au	120 ppm		

4.1.3.3 Copper Lines

The effect of a cyanide matrix on copper emissions is very small. The detection limit of the analyte line at 123.6 nm was raised by a factor of 4 while those of 224.7, 324.8 nm, 327.4 nm and 521.8 nm remained unchanged. The LDR of 3 orders of magnitude were retained. The precision of the lines either improved or remained comparable. The BEC of the lines were raised by the cyanide matrix. Table 6 summarizes the characteristics of the copper emission liness.

None of the interferents investigated resulted in a significant signal at the copper 213,6 nm and 224.7 nm lines. Niobium causes a small interference at 324.8 nm while 327.4 nm experiences interference by uranium and thorium. A large number of elements interfere with 521.8 nm, most notably Ti, Mo, Al and Cr. Table 6 also lists the results of the interferent study.

The spectral lines at 213.6 and 224.7 nm are recommended for copper analysis. The absence of interferences and large LDR are the advantages these two lines hold. However, if an accurate analysis is required for copper levels less than 1 ppm, the emission lines at 324.8 nm and 327.4 nm would be recommended.

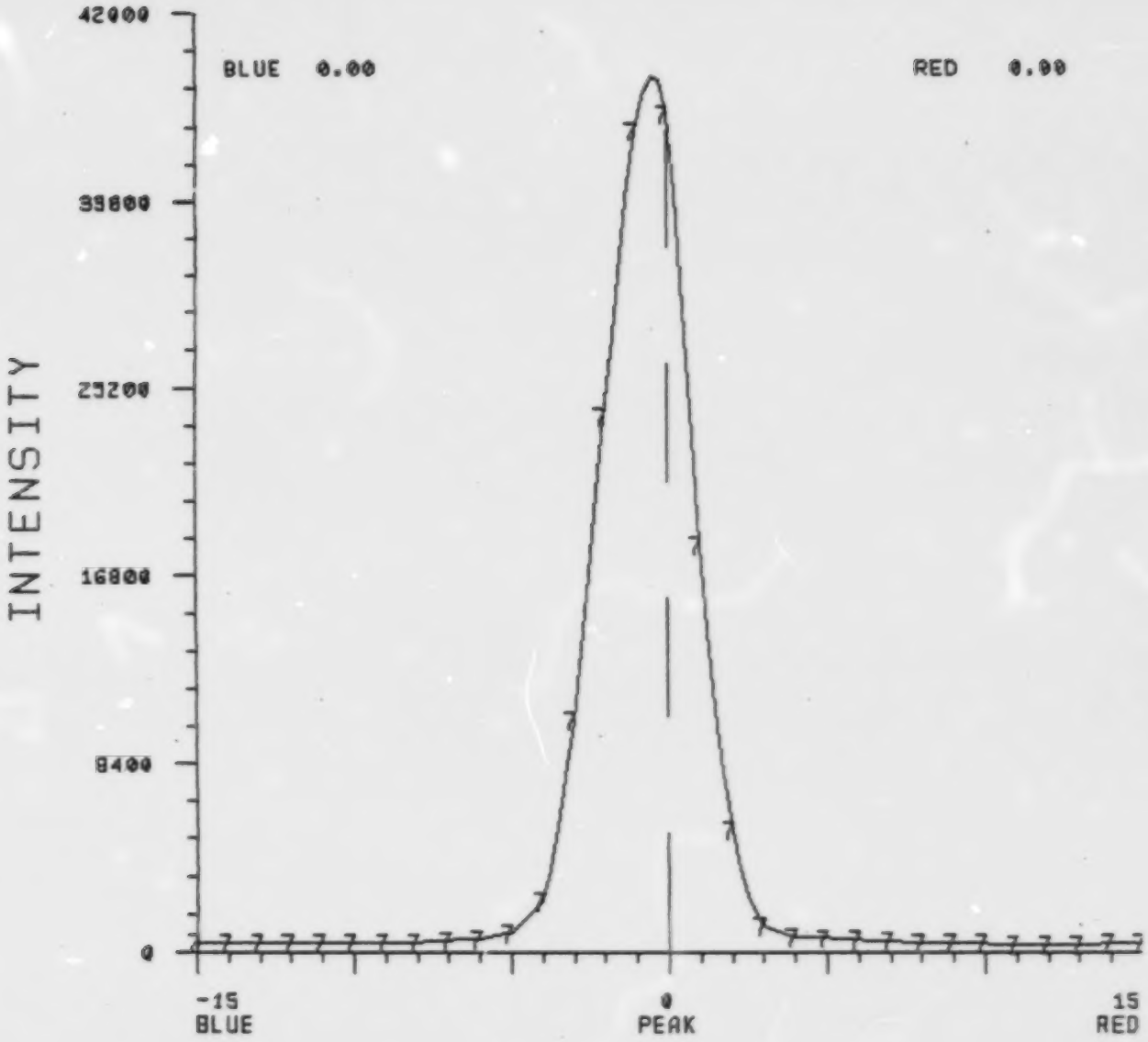
TABLE 6

Summary of Cu Line Characteristics

Line nm	Major Interferent	Analyte ppm	Linearity	Limit of Det^{n}	BEC	Precision
213.6	---	---	.4-1000 ppm	0.04	3.5	0.53
224.7	---	---	.4-1000 ppm	0.04	0.33	0.41
324.8	Nb	1.52	.02-10 ppm	0.002	0.16	0.90
327.4	U	.73	.07-10 ppm	0.007	0.21	0.69
	Th	2.9				
521.8	Mo	2.0	1-1000 ppm	0.11		0.51
	Al	1.0				
	Ba	1.0				
	U	5.7				
	Th	2.8				
	Ti	16.1				
	V	5.2				
	Cr	1.6				
	Nb	3.7				

The profile of copper emission at 213.6 nm plotted in Figure 7 shows that no interelement spectral interferences are present.

Figure 7 Cu 213.6 nm Wavelength Profile



Matrix Composition

Cu	1000 ppm	Ag	20 ppm
Fe	500 ppm	Na	3300 ppm
Zn	10 ppm	Ca	1000 ppm
Au	120 ppm		

4.1.3.4 Iron Lines

The cyanide matrix caused a decrease in the LDR for the analyte line at 238.2 nm. A deviation from linearity which exeeded 10% occurred between 200 and 300 ppm for the cyanide matrix while linearity was maintained to 1000 ppm in an acid solution. The limit of detection and background equivalent counts were comparable for the cyanide and acid matrices at this wavelength.

The limit of detection for the emission at 259.9 nm was increased from 0.007 to 0.02 ppm by the cyanide matrix. This resulted in a decrease in the LDR, however, the upper limit of 1000 ppm was maintained. The precision is comparable in either acid or cyanide matrices.

The LDR of the iron emission at 372.0 was reduced by 2 orders of magnitude to 0.1 ppm - 200 ppm. The detection limit was doubled while the BEC quadrupled. The precision remain unchanged.

A number of minor interferences are present on all lines. However, since iron is usually present in concentration much higher than the majority of other interferents, their effect on the analysis would be negligible.

The iron emission line at 259.9 nm is recommended due to its large LDR which would encompass practically all levels of iron encountered in gold millings.

The analyte line characteristics are tabulated in Table 7.

TABLE 7

Summary of Fe Line Characteristics

Line nm	Major Inferent	Analyte ppm	Linearity	Limit of Det^{n}	BEC	Precision
238.2	Au	0.6	0.1-200	0.01	0.4	0.67
	Ni	0.5				
	Re	0.5				
	Ti	1.1				
	Pt	1.3				
259.9	Au	0.5	0.2-1000	0.02	0.4	0.50
	Ti	1.0				
	U	0.5				
372.0	Au	0.6	0.1-200	0.01	0.4	0.99
	Mo	0.7				
	Ni	0.5				
	U	1.5				
	Ti	1.7				
	V	0.5				
	Nb	0.7				

Figure 8 shows the clean profile of Fe 259.9 nm with no spectral interferences from Cu, Zn, Ca, Na, Au or Ag.

4.1.3.5 Zinc Lines

Zinc often being the base metal of lowest occurring concentration in gold milling solucions, seldom reaches 100 ppm. If the emission line was linear between 0 and 100 ppm, a 200 ppm standard was analyzed and, if its assay was within 10% linearity, the upper limit of the LDR was reported as greater than 100 ppm.

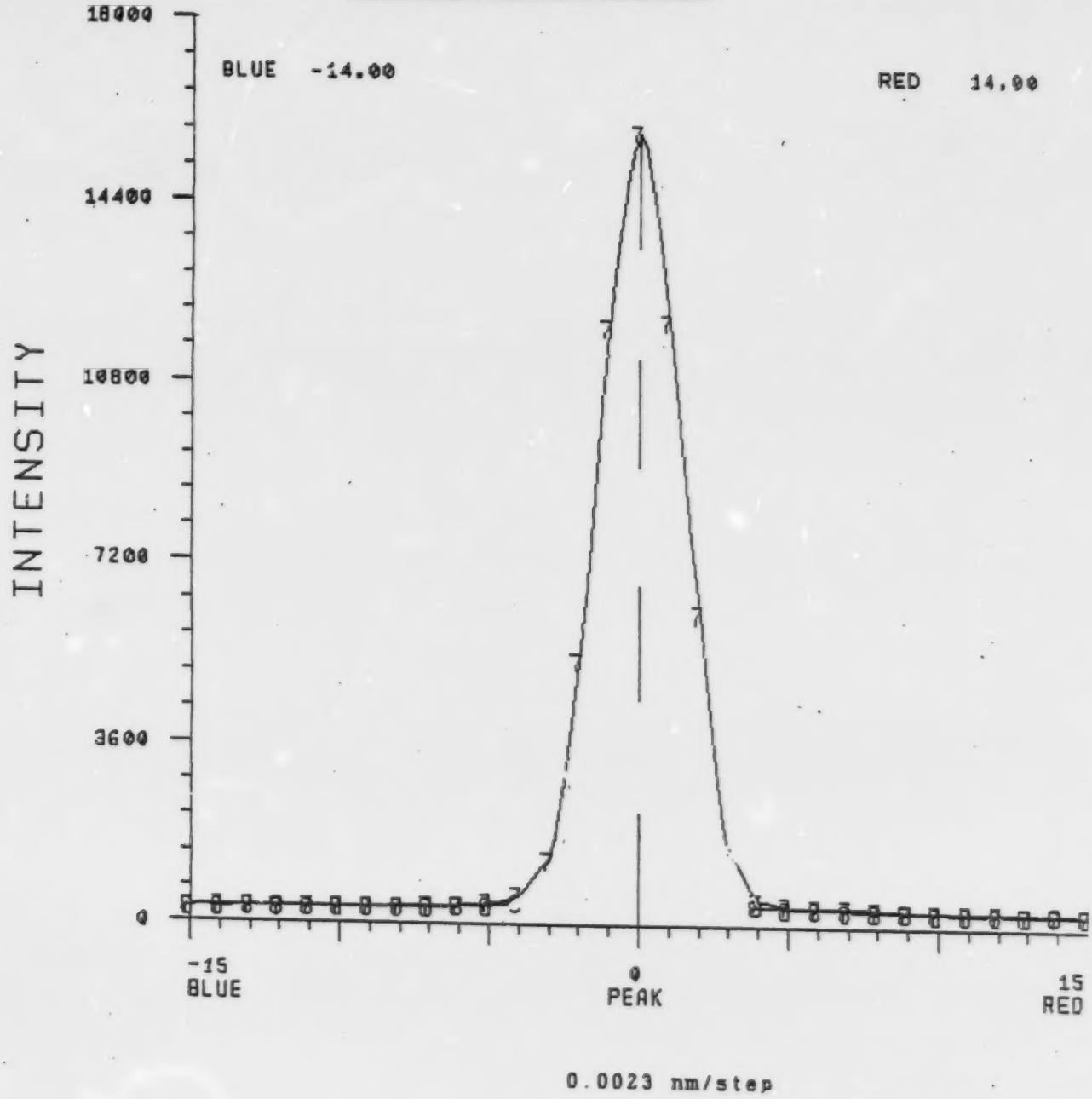
The effect of the cyanide matrix on the zinc emissions at 202.5 nm and 206.2 nm was small. The BEC and detection limits and precision increased by a factor of 2 or less. The upper limits of the LDR were greater than 100 ppm and the lower limits increased slightly.

At 213.9 nm, the LDR was halved with the upper limit falling from 10 to 5 ppm. The BEC and limit of detection remained comparable. A better precision resulted in the cyanide matrix.

No interferences were found at the 202.5 nm and 206.2 nm emissions. Nickel interfered significantly at 213.9 nm.

FIGURE 8

Fe 259.9 nm Wavelength Profile



Matrix Composition

Cu	1000 ppm	Ag	20 ppm
Fe	500 ppm	Na	3300 ppm
Zn	10 ppm	Ca	1000 ppm
Au	120 ppm		

The emission lines of 202.5 nm and 206.2 nm are recommended due to the absence of interferents and linear dynamic ranges which would encompass the zinc levels commonly found in cyanide process solutions.

Table 8 contains the line characteristics for the zinc emission lines investigated.

TABLE 8

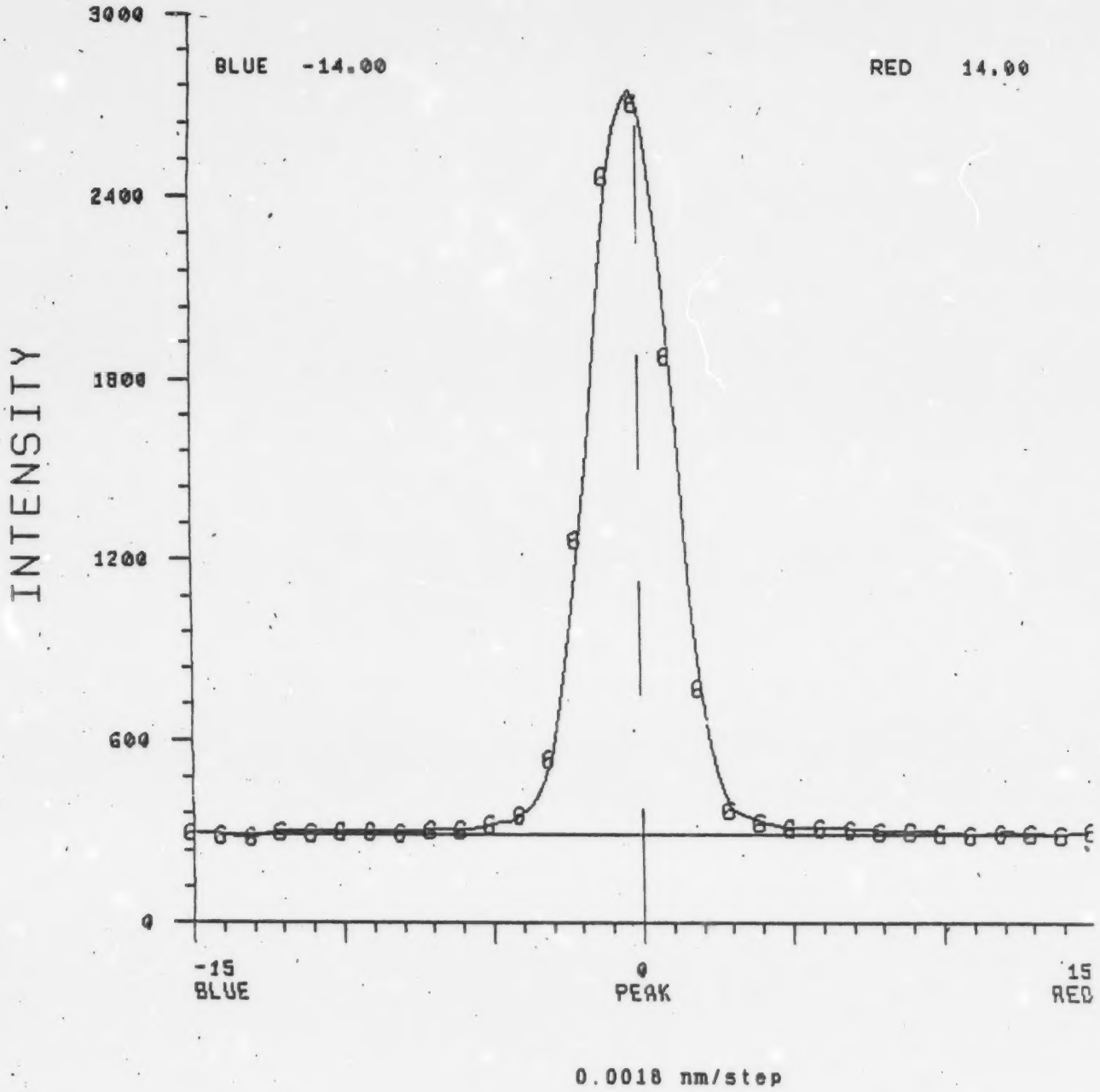
Summary of Zinc Line Characteristics

Line nm	Major Interferent	Analyte ppm	Linearity	Limit of Det^{n}	BEC	Precision
202.5	--	--	0.1 > 100	0.01	0.8	0.35
206.2	--	--	0.3 > 100	0.03	1.0	0.53
213.9	Ni	2.6	0.3 - 5	0.03	0.5	0.50

The emission profile of 10 ppm Zn in the matrix for leach 2 is presented in Figure 9 . A clean background is apparent with no spectral interferences from the high levels of Cu, Fe, Au, Ag, Ca and Na.

FIGURE 9

Zn 202.6 nm - Wavelength Profile



Matrix Composition

Cu	1000 ppm	Ag	20 ppm
Fe	500 ppm	Na	3300 ppm
Zn	10 ppm	Ca	1000 ppm
Au	120 ppm		

4.1.3.6 Arsenic Lines

The detection limit of the arsenic emission at 193.7 nm was raised to 0.2 ppm with a cyanide matrix. As a result the linear dynamic range was decreased to 2 - 100 ppm. Though this line is noted as plasma sensitive, the upper limit of the LDR did not fall in comparison to the acid matrix. The BEC doubled and the precision remained comparable.

The upper limit of the LDR of the emission at 228.8 nm decreased slightly in the cyanide matrix, while the lower end increased.

The LDR was determined to be 2 - 50 ppm in the cyanide matrix. The BEC tripled to 15 ppm representing a very high background. The precision remained unchanged at 0.9%.

There is a large spectral interference from cadmium on 228.8 nm as well as several other small interferences. The emission at 193.7 nm is interfered with by vanadium and platinum.

Table 9 summarizes the arsenic line characteristics.

TABLE 9

Summary of As Line Characteristics

Line nm	Major Interferent	Analyte ppm	Linearity	Limit of Det^{n}	BEC	Precision
193.7	V	1.0	2-100 ppm	0.2	9	0.98
	Pt	1.3				
228.8	Co	1.1	2-50	0.2	15	0.91
	Ni	1.1				
	V	9.8				
	Cd	>20				

Two arsenic standards were made by diluting 10 ppm As with the previously prepared mixed standards containing the metal interferents, calcium and sodium. This was done in order to have a matrix resembling the gold milling solution. The 1 ppm As standard was prepared in standard 3 as described in Table 18. The 2 ppm As standard was prepared in standard 1 which is also described in Table 18.

The arsenic standards were scanned on the emission lines 193.7 nm and 228.8 nm. Plots of these scans are presented in Figures 10-13. Both lines had extremely high background with a S/N ratio of at best 1.5. There are multiple peaks on either side of both lines.

At 193.7 nm these interferent peaks are of greater intensity than the arsenic peak. The scan of 1 ppm As in Standard 3 indicates that a major spectral interference occurs at the peak. The arsenic peak shows as a shoulder of the nearby broad interfering peak. At 2 ppm, the arsenic peak has merged with the interferent peak.

The emission at As 228.8 nm is cleaner than that at As 193.7 nm. It is the most intense peak in the window. However, a spectral interference is again apparent, showing as a shoulder on the arsenic peak. The S/N ratio is approximately 2. This spectral interference can however be corrected using a suitable background correction.

The scans indicate the analysis of arsenic in cyanide solutions is indeed a problem. The emission at 193.7 nm is marked by overlapping interference which eliminates this wavelength as an analyte line. Background correction could not be applied since the analyte peak is not distinguishable from the interfering peak.

FIGURE 10 As 193.7 Wavelength Profile of 1 ppm As

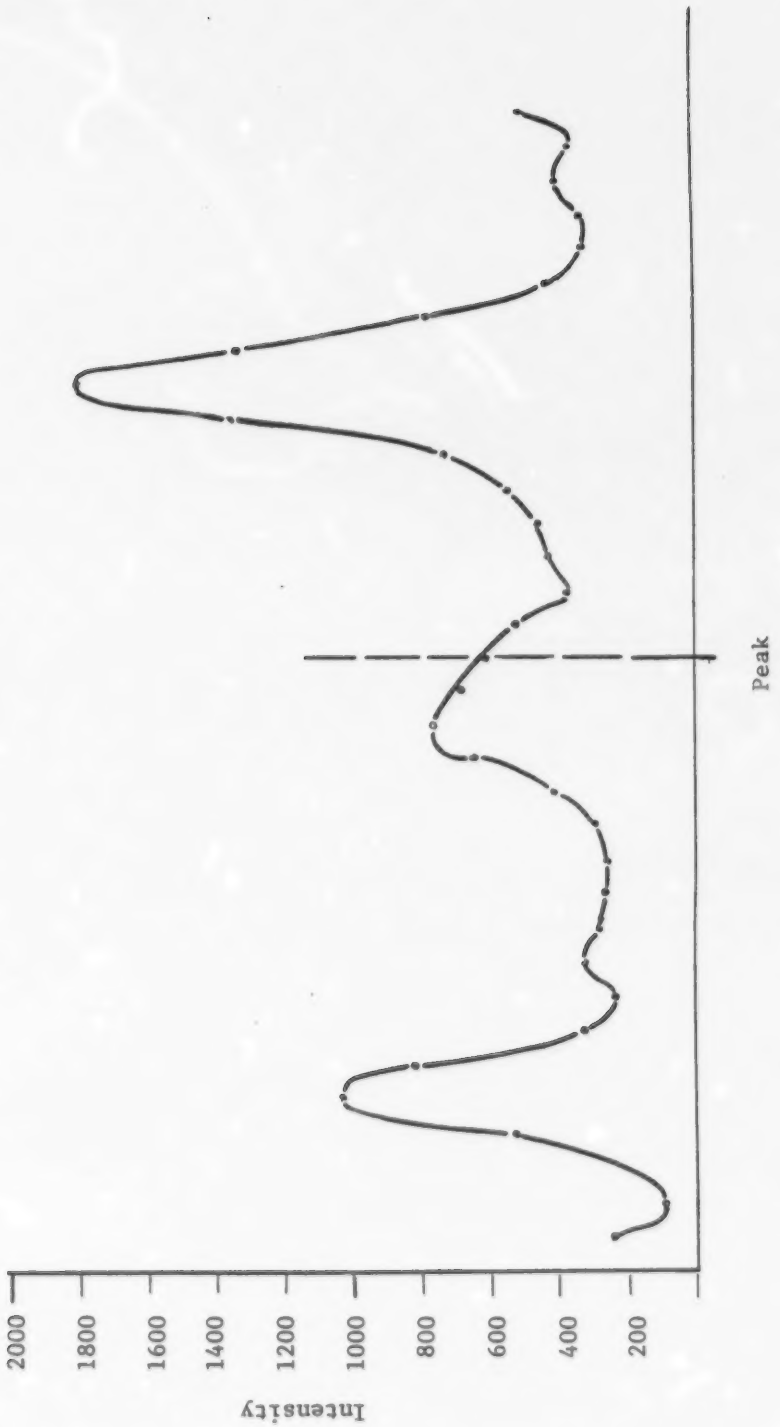


FIGURE 11 As 193.7 - Wavelength Profile of 2 ppm As

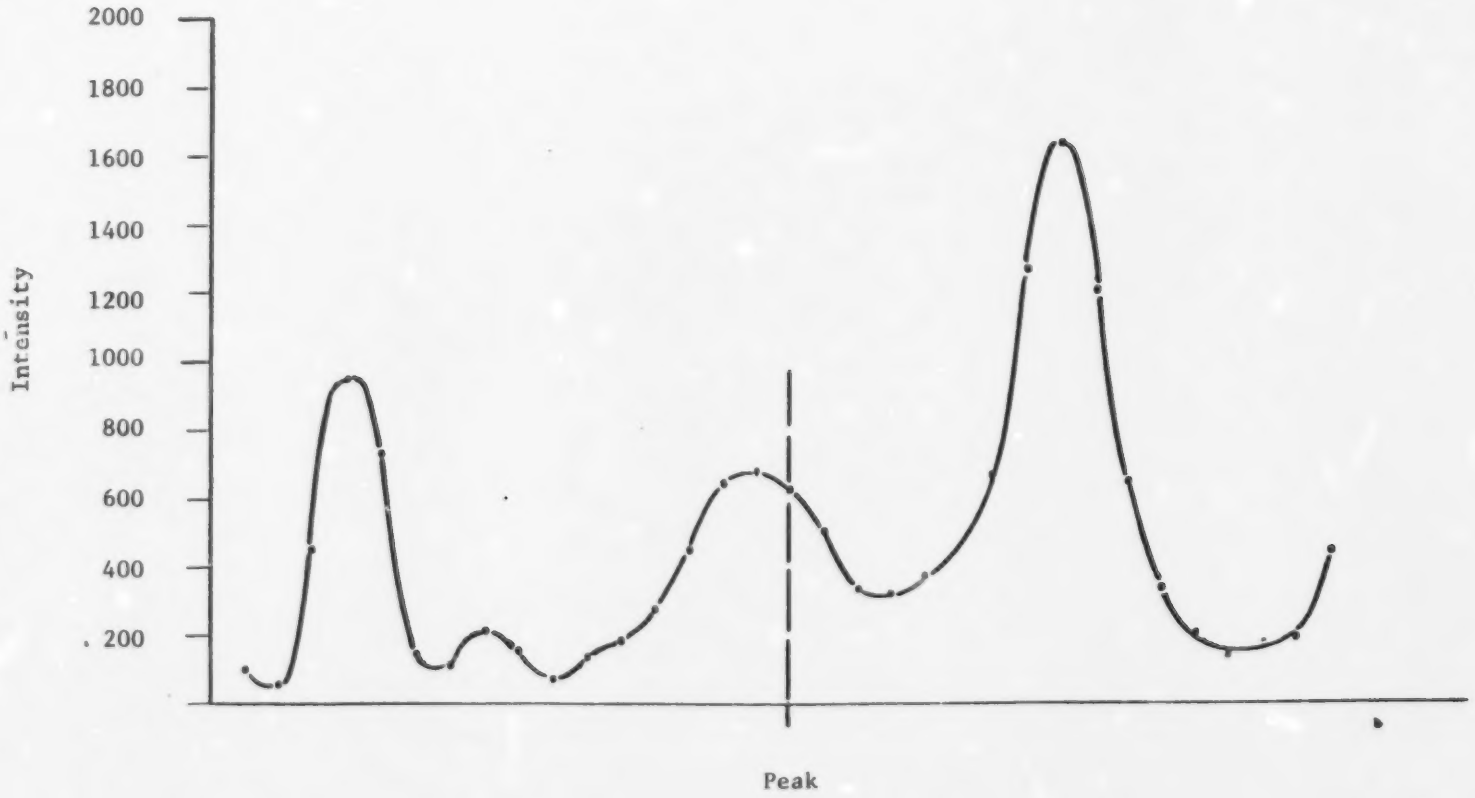


FIGURE 12 As 228.8 - Wavelength Profile of 1 ppm As

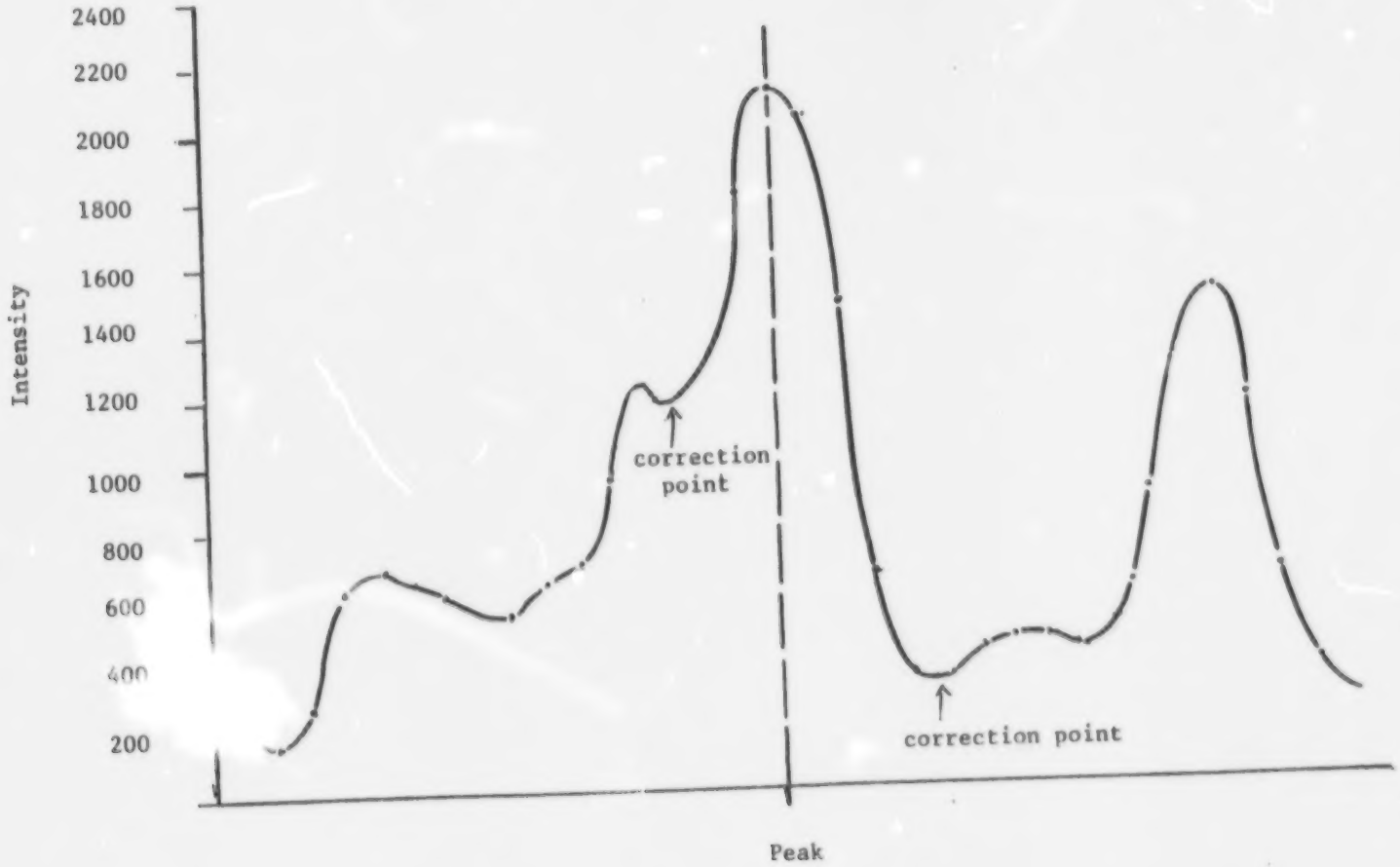
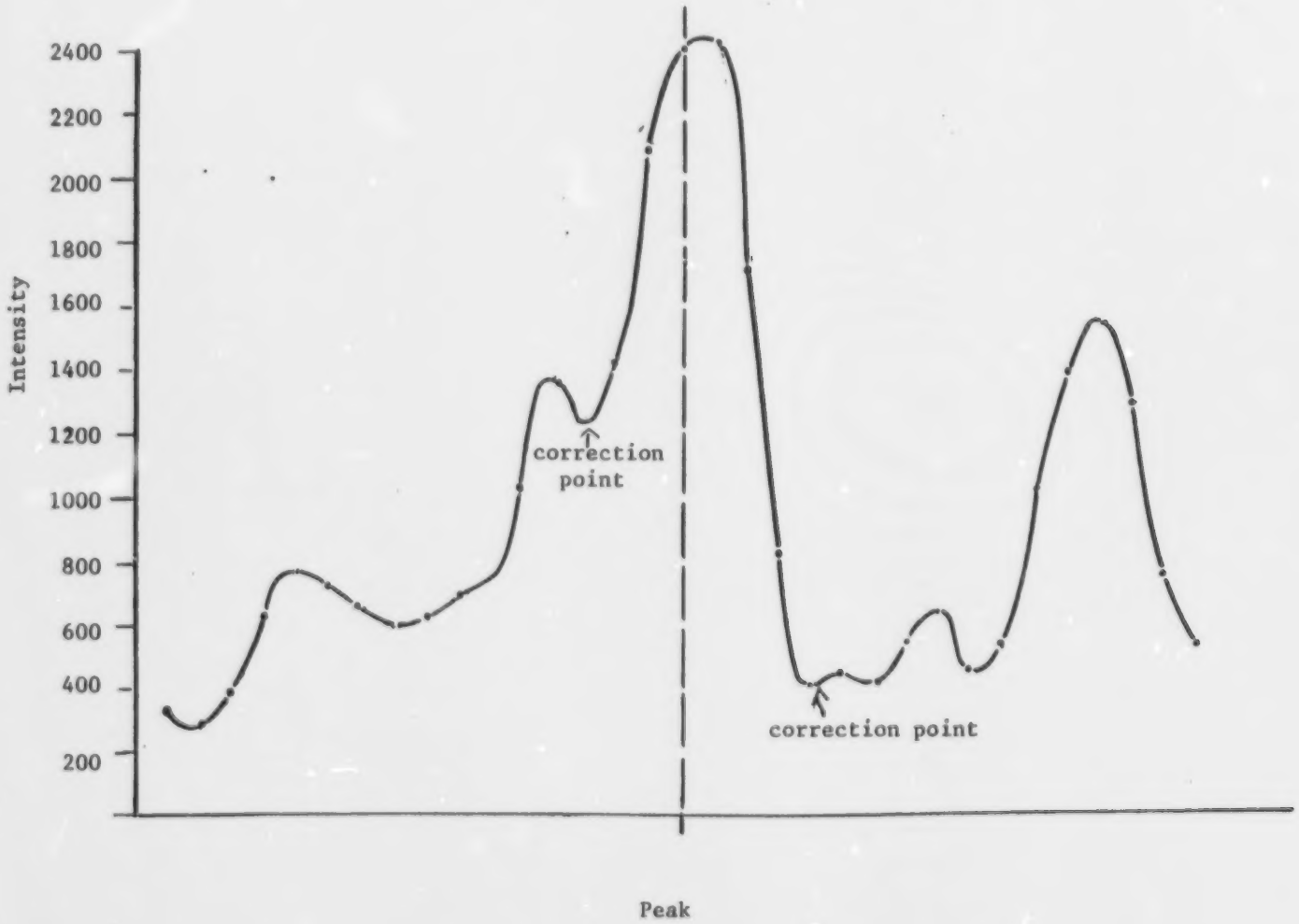


FIGURE 13 As 228.8 - Wavelength Profile of 2 ppm As



Neither of these two lines can be recommended for the direct analysis of arsenic in cyanide solutions due to the interferences and high background experienced. Pretreatment of the sample to eliminate interferences and possibly concentrate the arsenic is highly recommended.

4.1.3.7 Mercury Lines

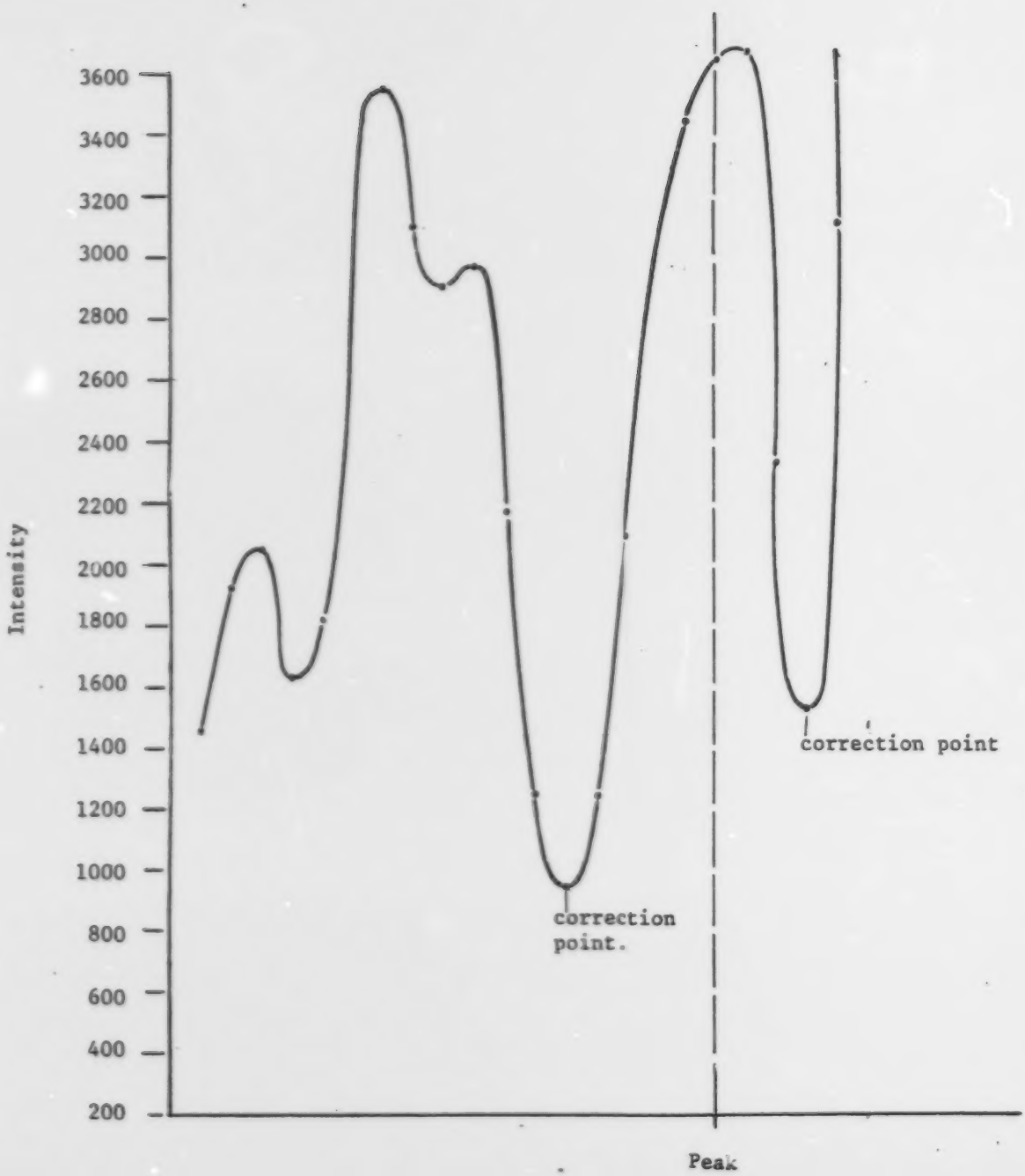
The analysis of mercury by direct current plasma is also severely hampered by the cyanide matrix. High backgrounds and limit of detections are observed at both analyte lines investigated when high calcium and sodium are present.

The limit of detection of the emission at 253.7 nm tripled to 0.06 mg/l. The linear dynamic range of 0.6 ppm to greater than 100 ppm is sufficient for mill solution analysis. A precision of 0.46% was obtained with a BEC of 2.5.

A detection limit of 6.4 mg/l and a linear dynamic range of 10 - 100 mg/l for the emission at 546.1 nm causes this line to be unsuitable for analysis of mercury in cyanide solution. The BEC of 130 makes the peaking of the monochromator extremely difficult. Further investigation of this line was not pursued.

FIGURE 14

Hg 253.7 - Wavelength profile of 1 ppm. Hg.



Major interferences from aluminum, platinum and cobalt are present at 253.7 nm. A relatively small interference from iron would be significant in the determination of low level mercury due to the high concentration of iron normally present in milling solutions.

The wavelength profile of 253.7 nm, Figure 14 shows many interfering peaks caused by the interferent and matrix matched standard. Due to the high background and large number of intense background peaks at 253.7 nm, analysis of mercury in a cyanide solution cannot be recommended utilizing this analyte line.

Table 10 summarizes the characteristics of the investigated mercury lines, neither of which are recommended for the direct determination of mercury in milling solutions.

TABLE 10

Summary of Hg Line Characteristics

Line nm	Major Interferent	Analyte ppm	Linearity	Limit of Det^{n}	BEC	Precision
253.7	Fe	0.5	0.5 ->100	0.06	2.5	0.46
	Co	20				
	Al	2				
	Pt	5				
546.1			10 - 100	6.4 ppm	1.30	0.91

4.2 Cyanide Matrix Effects

4.2.1 Effect of Sodium on Gold Determinations

Standards were prepared containing 25, 60 and 100 ppm of gold in combination with 0, 0.1, 0.5, 1.0, 2.0 and 5.0 gpl sodium. The standards were stabilized with 5% HCl. The concentrations of gold were chosen to span the linear range of the emission lines. These standards were used to determine the enhancement effect of sodium on the gold emissions.

The instrument was calibrated with the blank sodium/blank gold standard and the blank sodium/100 ppm gold standard. The standards containing sodium were then analyzed against the blank sodium standards to determine the effect of sodium.

4.2.1.1 Sodium Effect on Au 242.8

Table 11 contains the assays of the various gold and sodium combinations. The standard curves for each sodium level are plotted in Figure 15.

TABLE 11

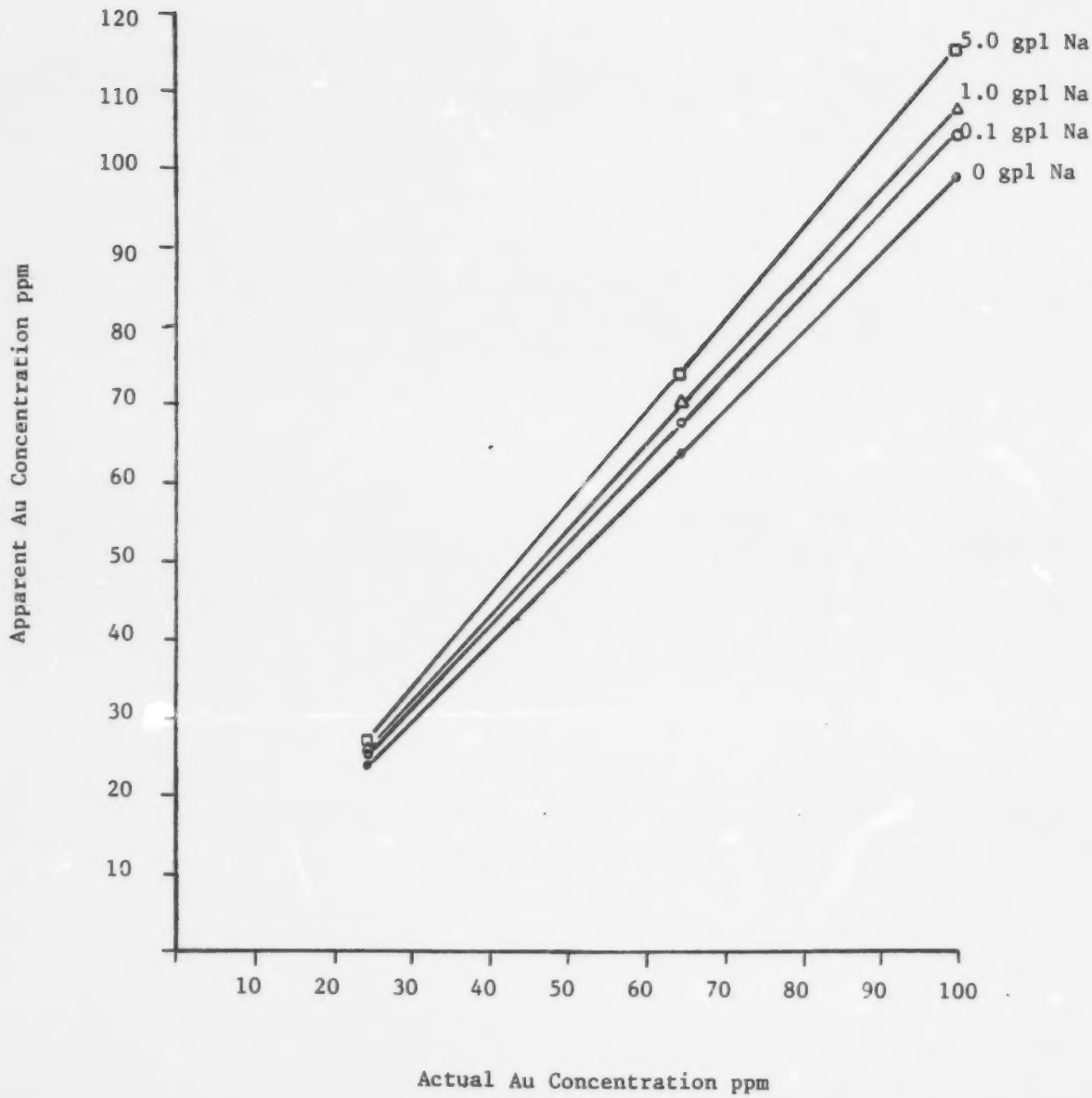
Sodium Enhancement of Au 242.8 nm

Na Level gpl	20 ppm Au		60 ppm Au		100 ppm Au	
	Assay	% Enhancement	Assay	% Enhancement	Assay	% Enhancement
0.0	24.0	0.0	64.0	0.0	100	0.0
0.1	25.8	7.5	67.6	5.6	105	5.0
0.5	26.1	8.9	68.9	7.7	105	5.0
1.0	25.2	5.0	71.3	11.4	108	8.0
2.0	25.6	6.6	72.7	13.6	110	10.0
5.0	26.4	10.0	74.1	15.8	116	16.0

An enhancement of the gold signal at 242.8 nm occurs in the presence of sodium. The signal resulting from 100 ppm gold is enhanced 15% in the presence of 5 gpl Na. The sodium effect is apparent even at the low level of 0.1 gpl Na causing the gold determinations to increase by an average of 6%.

The degree of enhancement does not appear to be linear with increasing sodium concentration. As well, a limit to the enhancement is not reached by 5 gpl Na, which is within concentration range of typical gold milling solutions.

FIGURE 15 - Effect of Na Concentration on Au 242.8 nm.



4.2.1.2 Sodium Effect on 267.6 nm

Table 12 shows the assays for the standard curves obtained with differing sodium levels at the gold emission wavelength of 267.6 nm. The sodium spiked standards varied little from the blank sodium standards. The variance of less than 5% indicates that this line has little dependence on the sodium level.

TABLE 12

Sodium Enahncement on Au 267.6 nm

Na Level gpl	20 ppm Au Assay	% Enhancement	60 ppm Au Assay	% Enhancement	100 ppm Au Assay	% Enghancement
0.0	21.8	0.0	62.7	0.0	100	0.0
0.1	22.6	3.7	63.9	1.9	100	nil
0.5	22.9	5.1	64.8	1.7	98.2	(0.8)
1.0	22.6	3.7	65.8	3.4	101	1.0
5.0	22.7	4.1	65.4	4.3	105	5.0

4.2.2 Effect of Calcium on Gold Determinations

Standard solutions were prepared containing 25, 60 and 100 ppm gold and spiked with each of 0.01, 0.5, 1.0, 2.0 and 5.0 gpl Ca. The solutions were stabilized with 5% HCl.

The instrument was calibrated using the blank calcium/100 ppm gold solution as the high standard. The low standard was set with 5% HCl. The standards containing calcium were then analyzed against the blank calcium standards.

4.2.2.1 Calcium Effect on Au 242.8 nm.

Table 13 shows the analyses of the solutions at the Au 242.8 nm.

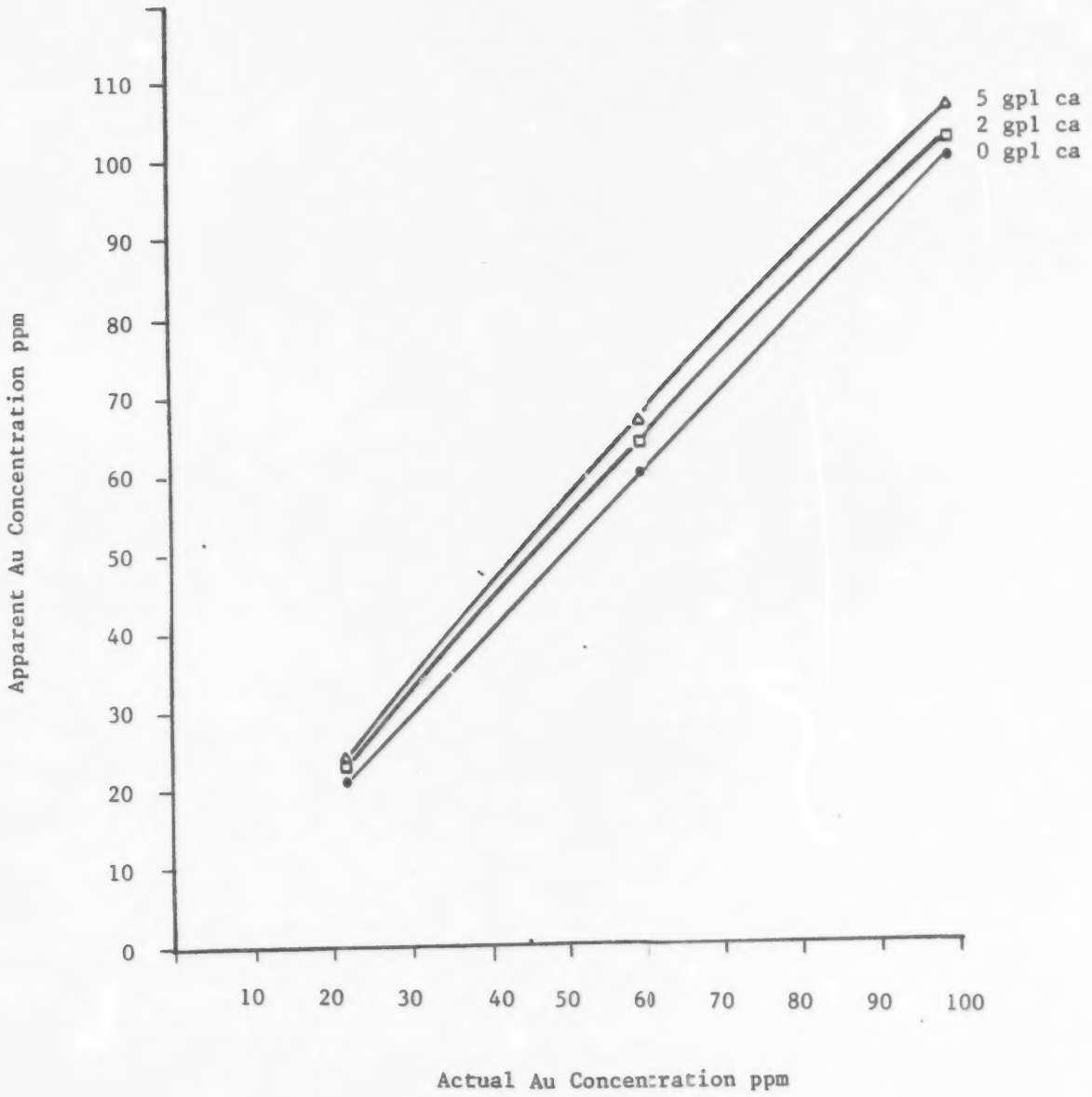
TABLE 13

Calcium Effect on Au 242.8 nm

gpl Ca	20 ppm Au Assay	% Error	60 ppm Au Assay	% Error	100 ppm Au Assay	% Error
0	21.8	0.0	60.5	0.0	99.4	0.0
0.1	21.9	nil	62.0	6.5	100.0	nil
0.5	20.8	nil	62.0	3.3	96.6	nil
1.0	22.2	nil	64.7	7.8	102.0	2
2.0	23.3	5.9	67.6	12.7	103.0	3
5.0	23.9	8.6	67.9	13.2	107.0	7

The standard curves for 0.1 and 5 gpl are plotted in Figure 16.

FIGURE 16 - Effect of Ca Concentration on Au 242.8 nm.



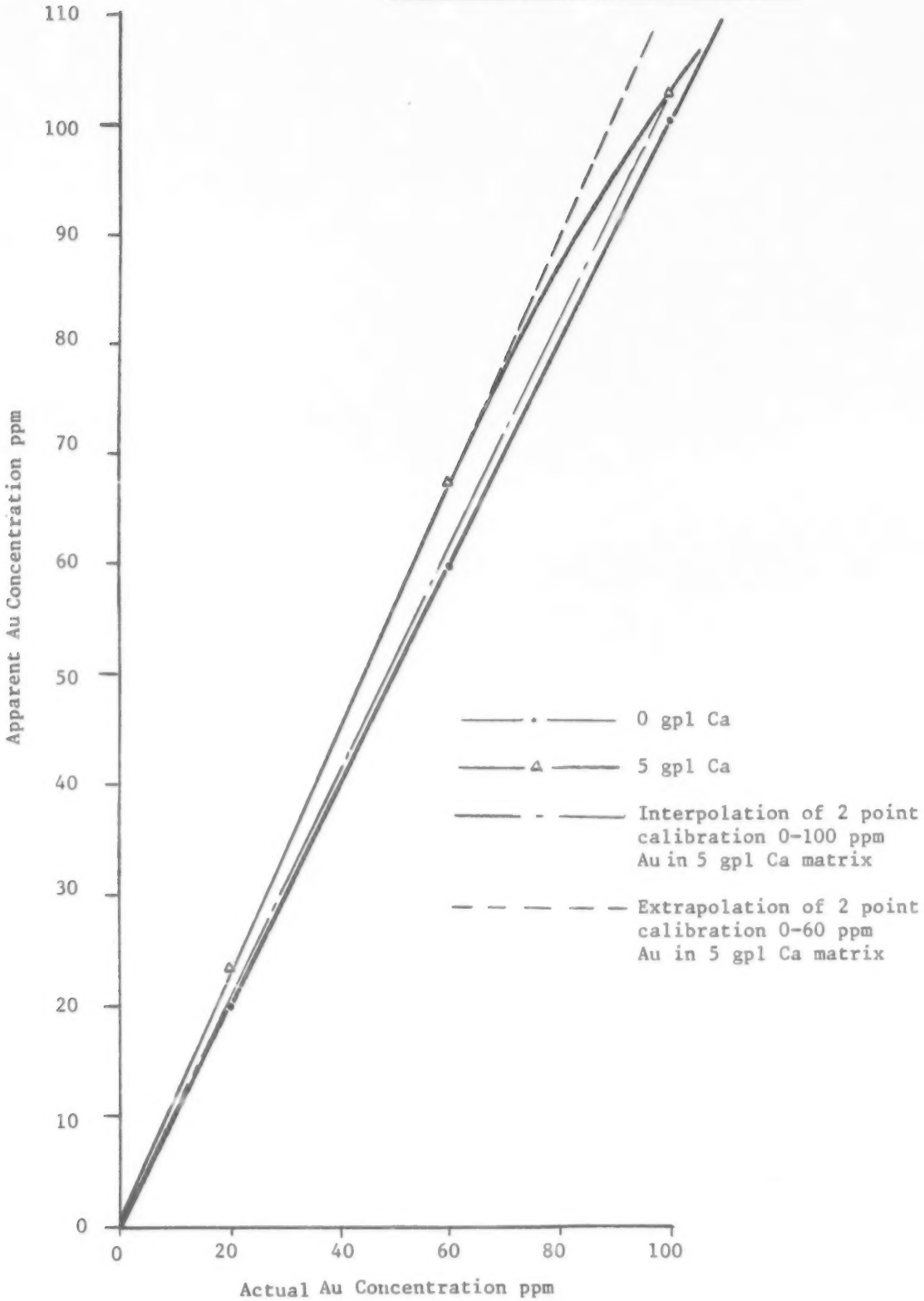
The effect of calcium seems to be twofold. Calcium levels of 2 gpl and higher resulted in apparent enhancement of the gold emission. The second, and more important effect, is a loss of linearity which is apparent even at the low level of 0.1 gpl Ca. This loss of linearity could cause inaccurate assays even if matrix matching has been employed due to the nature of the two point calibration method. If the calibration is set between two points where linearity is not maintained, a falsely low assay would result. If the calibration is set on the linear portion of the curve, interpolated results would be accurate. However, extrapolated results would be falsely high.

To illustrate the effect of the loss of linearity, the standard curves with 2 gpl Ca and 0 gpl Ca have been plotted in Figure 18 . Two point calibration curves have also been plotted, one between 0 and 60 ppm Au in 2 gpl Ca and another between 0 and 100 ppm Au in 2 gpl Ca. Table 14 lists the errors resulting from reading a 100 ppm Au and 2 gpl Ca sample on the various calibration curves.

TABLE 14 - Potential Errors as a Result of Calcium Influences on the Calibration Curve.

Standards used in Calibration		100 ppm Au % error	80 ppm Au % error	60 ppm Au % error
low	high			
0 ppm Au/0 gpl Ca	100 ppm Au/0 gpl Ca	3	9	13
0 ppm Au/2 gpl Ca	60 ppm Au/2 gpl Ca	8	2	nil
0 ppm Au/2 gpl Ca	100 ppm Au/2 gpl Ca	nil	6	(8)

FIGURE 17 Potential Errors as a Result of Ca Influences on the Calibration Curve



4.2.2.2 Calcium Effect on 267.6 nm

As the data in Table 15 indicates, an enhancement and loss of linearity of the emission at Au 267.6 nm results from levels of calcium equal to or greater than 2.0 gpl. Gold milling solutions typically contain less than this level of calcium due to its limited solubility. The loss of linearity at low levels of calcium as seen with the emission at Au 242.8 nm is not apparent here. It seems that the emission at 267.6 nm is less sensitive to both calcium and sodium effects.

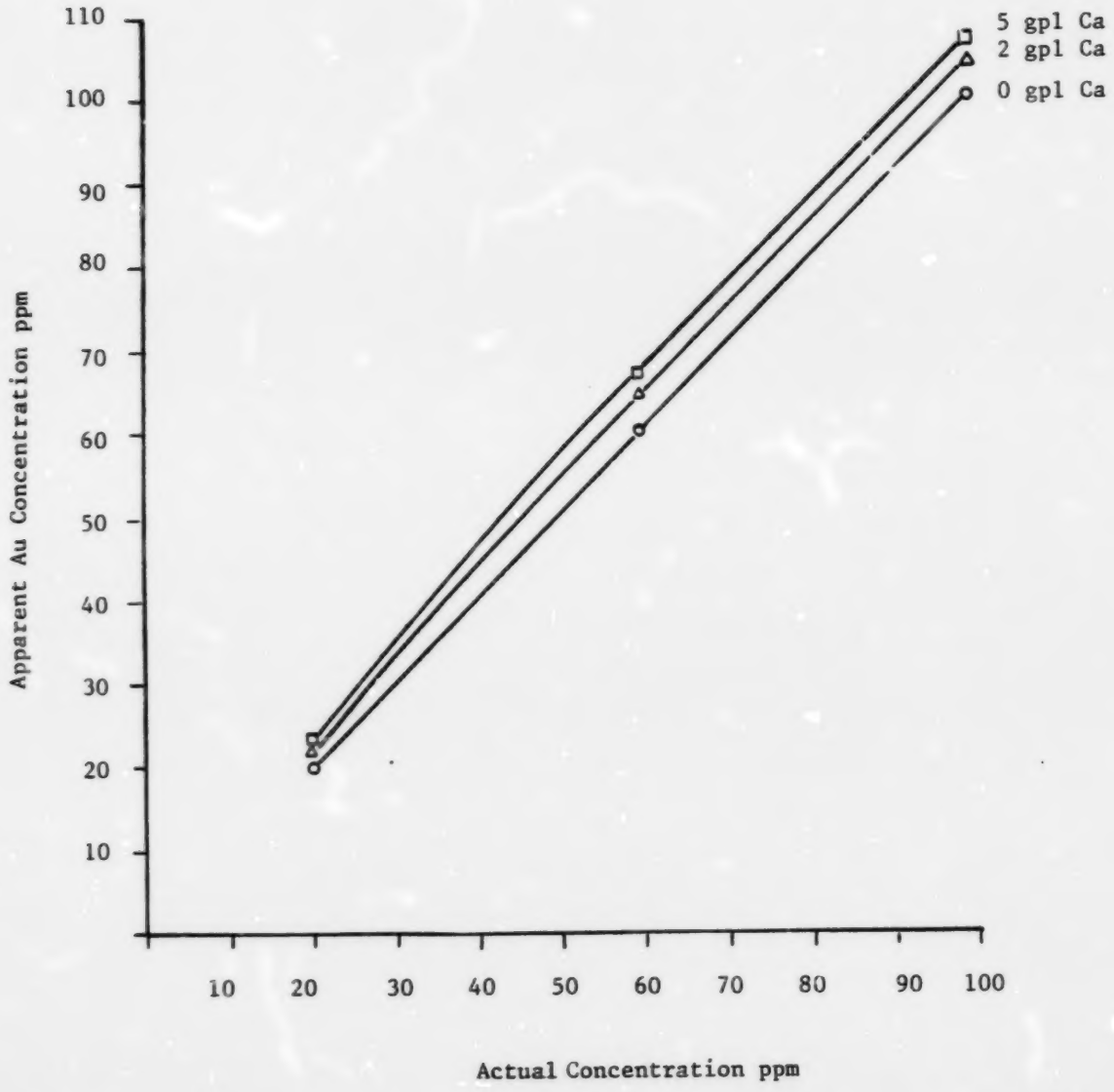
TABLE 15

Calcium Effect on Au 267.6 nm

	20 ppm Au		60 ppm Au		100 ppm Au	
gpl Ca	Assay	% Error	Assay	% Error	Assay	% Error
0.0	20.7	nil	59.8	nil	98.5	nil
0.1	21.2	nil	60.0	nil	99.5	nil
0.5	19.8	nil	60.6	nil	98.7	nil
1.0	20.7	nil	60.8	nil	101.0	nil
2.0	22.5	nil	64.9	8.0	104.0	4.0
5.0	23.2	6.0	66.0	11.0	107.0	7.0

Figure 18 contains the plots of the 0, 2 and 5 gpl Ca curves showing the enhancement and the slight loss of linearity.

FIGURE 18 - Effect of Ca Concentration on Au 267. 6 nm.



4.3 Process Solution Analysis

4.3.1 Leaching of Gold Ores

Five gold ores were chosen for leaching on the basis of differing mineralization and lead grade. A representative 500 g charge was split from the sample for leaching purposes. The ores were leached with cyanide levels previously determined to be optimum for each ore. Similarly, the particle size of the ore and lime addition for pH control varied for each ore, as previously determined to be optimum. In this way, the resulting leach solutions were truly indicative of the actual processes that would be employed for each ore.

Two flotation concentrates were also leached with the above considerations.

The level of cyanide and lime were monitored on a regular basis and maintained at optimum levels for highest extraction. The sample aliquots taken throughout the leach for the filtration of lime and free cyanide were combined for subsequent analysis.

Table 16 lists the head assay and reagent consumptions for each gold ore sample.

TABLE 16 Head Assays and Reagent Consumptions for Gold Ore Leaching Tests

Leach No.	Head Grade g/t	Consumption kg/t Lime (CaO)	Cyanide (NaCN)
1	64.5	1.1	9.1
2	179.3	2.8	6.9
3	0.51	0.8	3.0
4	3.50	6.8	4.3
5	53.1	8.4	15.3
6	3.43	4.3	1.6
7	5.01	13.7	6.9

The filtrate from the leach, the water used to wash the residue and the filtration solution were sampled and represent the milling solutions for analysis. Head and residue samples were prepared to a minimum of -100 mesh and analyzed for gold by fire-assay using the lead collection method with DCP finish following acid dissolution of the precious metal bead. This provided the data required for mass balance calulation.

4.3.2 Qualitative Analysis of Leach Solutions.

A 2 dimensional spectrum was generated from the mono-chromator and recorded on polaroid film. Each light spot on the photograph corresponds to the order and wavelength of emission which is characteristic of an element. A comparison of the sample spectral pattern with standard emission templates, allows the identification of elements present in solution.

The elements detected in the qualitative determinations of the filtrates for each leach are listed in the following Table 17.

TABLE 17

Qualitative Identification of Elements Present in Leach Solutions

Filtrate No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Au	Au	Au	Au	Au	Au	Au
Ca	Ca	Ca	Ca	Ca	Ca	Ca
Cu	Cu	Cu	Cu	Cu	Cu	Cu
Fe	Fe	Fe	Fe	Fe	Fe	Fe
Mg	--	Mg	Mg	Mg	--	--
Mn	--	--	--	--	--	--
Na	Na	Na	Na	Na	Na	Na
Zn	--	--	--	--	--	Zn
--	Sr	--	--	--	--	--
--	Ni	--	--	Ni	--	--
--	--	--	--	Ag	--	--

4.3.3 Quantitive Analysis of Leach Solutions

The solutions generated by the leaching of the various gold ores were analyzed for gold, silver, copper, iron and zinc. Mixed standards were prepared containing the approximate levels of the metals present. These approximate levels were obtained by aspirating the filtrate from each of the leaches at the recommended wavelengths for each metal. The calcium and sodium levels were approximated from the reagent additions throughout the leach. Since the solubility of lime is such that only 1 gpl Ca may exist in solution, any calcium above this level was assumed to have consumed during the leaching.

A mixed standard, both interferent and matrix matched, was therefore, prepared for each gold ore which contained the approximate levels of metals, calcium and sodium.

Three blanks were prepared for each standard. A 5% hydrochloric acid blank was utilized for analysis where no matrix or interferent matching was involved. A matrix blank was prepared with matched sodium and calcium levels. For interferent matched assays, a blank containing the appropriate levels of sodium, calcium, iron, copper, zinc and silver was prepared. Table 18 lists the levels of the elements in the standards for each of the leaches.

TABLE 18

Composition of Standards (ppm)

Element	1	2	3	4	5	6	7
Au	30	120	0.5	4	30	3	6
Cu	50	1000	40	50	1000	200	50
Zn	6	10	2	6	200	6	6
Fe	400	500	300	500	200	100	500
Ag	10	10	10	10	10	10	10
Ca	800	1000	60	1000	1000	1000	1000
Na	4400	3300	1400	2000	7000	800	5400

The assay of the various leach solutions were determined by different methods which are described below:

1. Atomic Absorption

The atomic absorption analysis was completed by an independent contract assay laboratory. Preconcentration and sample treatment was left to the discretion of the assayer.

2. Direct Current Plasma - No Matrix Matching (DCP-NMM)

The DC plasma spectrometer was calibrated with standards prepared in 5% hydrochloric acid. The purpose of this was to assess the effects of using A.A. type non-matrix matched acid standards on the accuracy of the analyses. No attempt to match matrices or interferents was made.

3. Direct Current Plasma - Matrix Matched (DC-MM)

The spectrometer was calibrated with the mixed standard, the preparation of which was previously described, and a matrix matched blank which contained the appropriate sodium and calcium levels.

4. Direct Current Plasma - Interferent and Matrix Matched (DCP-MM)

The mixed standard and the blank containing the interferents as well as the calcium and sodium were used for calibration.

4.3.3.1 Gold Determination

Methods 2 to 4 which utilize emission analysis were performed on the gold lines at 242.8 nm and 267.6 nm. The solids were

assayed by lead collection fire assay methods with a DCP finish on the precious metal bead.

For the purpose of data analysis, the mass balance for the leaching of each ore was calculated for the various analytical methods. A mass balance is a metallurgical accounting method whereby the sum of the milligrams of gold contained in the leach products (filtrate, wash, titration solution and residue) is compared to the milligrams of gold contained in the leach charge. This is the accepted method of determining the accuracy and precision of the metallurgical test.

A head is calculated by totalling the milligrams of gold in the leach products and the mass balance is expressed as the percentage of the calculated head over the assayed head. A deviation of ± 3 to 5% from the ideal 100% mass balance indicates the assay procedure does not contribute more error than that which is normally associated with sampling and testing errors. A mass balance is still considered acceptable with a ± 5-10% deviation. A deviation greater than 10% indicates that the analytical or sampling procedure is not adequate for meaningful analysis.

The analysis and mass balance calculations for each of the leaches are contained in Appendix II . Table 19 summarizes the mass balances for all the analytical techniques.

Prior to the discussion of the reliability of solution assay techniques, other sources of error in the mass balance should be discussed. A major possible source of error is in preparation of a leach charge which is representative of the head. Careful pulverization, rolling and splitting of the head sample is required to obtain a representative sample. Free gold in an ore often leads to serious sampling errors. The splitting of an assay sample from the residue also requires the care taken in splitting the leach charge. The fire assay of head and residue samples is also a source of error in the mass balance. The lead collection of gold in low grade ores may not be efficient, especially in the case of finely disseminated gold.

In general poor mass balances were obtained for leach Nos. 1, 3 and 7. The ore used in leach 3 had a very low head grade of 0.51 g/t. At this low level a small absolute error transposes into a large relative error. Leaches land 7 were flotation concentrates containing high concentration of sulphides. This high sulphide concentration may contribute to difficulties in sample preparation, leaching and fire assay analysis.

TABLE 19

Mass Balance Summary for the various Analytical Techniques (%)

		DCP-242.8 nm			DCP-267.6 nm		
Leach No.	AA	NMM	MM	IMM	NMM	MM	IMM
1	111	123	116	117.2	120	--	--
2		104.7	97.7	107.5	103.1	--	--
3	247	128	136	138	128	129	135
4	120	103.4	102.2	104.9	103.4	102.9	100.0
5	96	104.7	95.2	97.8	108.7	89.3	92.0
6	95	93.4	96.0	100.7	93.9	--	--
7	132	106.6	114.6	114.6	108.8	--	--

where AA = Atomic Absorption
NMM = Non Matrix Matched
MM = Matrix Matched
IMM = Interferent and Matrix Matched

Atomic absorption analysis gave acceptable mass balance for leach 5 and 6. For all other leaches, high mass balances were obtained. The larger error occurred in the analysis of the leach 3. This leach resulted in solutions containing between 0.1 and 0.5 mg/l Au. These low levels of gold are routinely preconcentrated prior to analysis by A.A. The mass balance of 247% by A.A. is greatly improved by DCP analysis (approximately 130%) where the solutions are aspirated directly into the plasma eliminating any error which may arise from preconcentration procedures.

The good agreement between the mass balances of the matrix matched and interferent matrix matched standards shows that spectral interference from silver, copper, iron and zinc are not present at the Au 242.8 nm and Au 267.6 nm lines. The clean scans of the emission profiles had indicated this also. Emission scans of the process solutions are strongly recommended, because in this way, potential interferent problems may be identified and the proper precautions of interferent matching and background corrections may be taken.

The investigation of the sodium and calcium effects on gold emissions utilizing synthetic solutions had indicated that a poor mass balance would result when matrix matching was not employed. In general, this was not observed in the analysis of the process solutions.

The study on calcium effects had indicated that significant enhancement and loss of linearity does not occur until calcium levels are on the order of 2 gpl or higher. The limited solubility of lime results in leach solutions which contain 1 gpl Ca or less. At these levels the calcium effect is low and significant error would not result.

Studies on synthetic gold solutions in a sodium matrix had indicated up to 15% error in the analysis of gold in the presence of high concentrations of gold. The good agreement between non-matrix matched analysis and analysis where the sodium level had been corrected for, indicates that this effect was not observed on these leach solutions. It is possible that a complex chemistry negates or suppresses the sodium effect. Regardless, solutions should be evaluated for sodium interferences by background profiling and by analyzing diluted samples on several portions of the calibration curve.

4.3.3.2 Silver and Base Metal Determinations

The base metal concentrations in the solutions from leach No. 4 and 5 were determined by the Spec VI fast sequential spectrometer model on each of the lines being investigated. The blanks were matrix matched with sodium and calcium. The data is summarized in Table 20.

Table 20 lists the assays for each solution on the various lines.

TABLE 20

Comparison of Silver and Base Metal Assays using various Analyte Lines

Analyte Line		Solution Assays (ppm)					
		5F	5W	4F	4W	3F	3W
Ag	328.1	2.95	.407	2.88	.403	.280	.113
	338.3	3.00	.381	2.91	.400	.270	.115
	546.5	ND	ND	ND	ND	ND	ND
Cu	213.6	613.2	98.4	2.44	.392	2.68	.222
	224.7	604.3	101.0	2.44	.398	2.56	.253
	324.8	>2000	>2000	ND	ND	3.21	.332
	327.4	>2000	651.5	7.85	1.42	2.72	.279
	521.8	640.4	111.9	2.4	3.46	2.28	ND
Fe	238.2	188.9	28.2	255.4	42.7	232.1	19.9
	259.9	187.5	29.8	257.2	44.4	216.9	19.7
	372.0	209.2	42.5	303.1	62.1	223.0	25.6
Zn	202.6	96.8	16.7			1.02	.075
	206.2	94.6	15.9			1.08	.078
	213.9	191.2	65.2			1.12	.072

where F = Filtrate solution
W = Wash Solution

4.3.3.2.1 Silver Assays

The silver concentrations determined at 328.1 nm and 338.3 nm agree within 5%. Both of these lines were recommended based on their linear dynamic range and low interferences.

The detection limit for silver 546.5 nm in a cyanide matrix was determined to be 0.1 ppm. However, no silver was detected in the solutions which range from 0.1 to 3.0 ppm. The large number of interferents on this line may lead to an even higher detection limit in an interferent matched matrix. The inadequacy of this line for determination of silver in cyanide solutions is clearly demonstrated.

4.3.3.2.2 Copper Assays

The assays obtained on the two recommended copper lines, 213.6 nm and 224.7 nm vary by less than 2% in comparison. The lack of linearity for 324.8 nm and 327.4 nm resulted in an "offscale" reading. The use of either of these lines would lead to erroneous assays. The emission at 521.8 nm gave fairly accurate readings however they varied ± 10% from the average of the other assays. It is of interest to note that the inaccurate assays were obtained from atom state emissions and the inaccuracy of the 7 gpl Na matrix of leach 5 is the highest.

4.3.3.2.3 Iron Assays

Good agreement was obtained between assays at 238.2 nm and 259.9 nm, the latter of which is the recommended line. Investigations

into the LDR of 238.2 nm showed that linearity was lost between 200 and 300 ppm. The assays indicate that linearity is maintained to 250 ppm since assays at this level are in agreement with those attained at 259.9 nm. The emission at 372.0 nm gave high readings in comparison to the assays obtained at the other wavelengths. As in the case of copper, these inaccuracies are more prominent in high sodium matrices and occur with an atom state emission. The error of the Fe 372.0 nm assays ranges from 10 to 50%.

4.3.3.2.4 Zinc Assays

The emissions at 202.5 nm and 206.2 nm resulted in zinc assays which are in agreement. Both these lines were recommended for their absence of interference and linearity. The zinc levels for 5F and 5W were well above the LDR of the emission wavelength 213.9 and largely erroneous assays resulted. However, 3F and 3W within the narrow LDR and a 10% was obtained.

4.3.3.3. Arsenic and Mercury Determinations

Scans of the analyte lines for mercury and arsenic have shown that preconcentration and removal of interferences would be necessary prior to analysis by direct current plasma. The typically low levels of these elements in cyanide solutions and commonly co-occurring metals result in an extremely high background and in some cases uncorrectable interferences. In order to obtain an accurate analysis, the arsenic and mercury should be removed from the cyanide matrix with little co-extraction of other metals. Separation techniques which are

commonly used include solvent extraction, distillation, hydride generation and cold vapour generation. Any of these techniques may potentially be applied as solution treatment prior to direct current analysis.

For arsenic analysis, the distillation of the trichloride and subsequent collection in hydrochloric acid would lead to an ideal matrix for emission analysis. The extraction of arsenic by a butanol/chloroform mixture would result in an organic solution amenable to analysis by direct current plasma. However, organic matrices do exhibit molecular bands and background which can be problematic in some cases. Attempts to extract arsenic from synthetic solutions containing 0.5, 1 and 2 ppm As, in 1 gpl Ca and 4 gpl Na were made. The extraction of 2 ppm As could not be detected. This could be due to a high limit of detection as a result of the organic matrix. If concentration of the arsenic was incorporated into the extraction procedure, this problem could be overcome. Qualitative analysis of the extract showed the presence of calcium which may be interfering in both the extraction and detection of arsenic.

Currently, several hydride generators are available which feed the hydrides directly into the plasma spectrometer. The major shortcoming of these devices is the necessity to integrate the signal over a period of time to account for signal trailing.

Plasma Therm markets a generator which reportedly exhibits the most promise of an accurate hydride assay when combined with a

direct current plasma rather than conventional atomic absorption apparatus.

The difficulty in obtaining an accurate analysis of mercury in cyanide solutions was seen in Figure 14. A cyanide matrix containing 1 ppm Hg and relatively low levels of interferents was scanned at Hg 253.7 nm. An intense peak on the high side of the wavelength is apparent. The intensity of this peak is at least 3 times the intensity of the mercury peak. On the low side, another interfering peak is present of the same intensity as the mercury peak.

The benefit of cold vapourization of the mercury from the cyanide solution and subsequent collection in a 6% W/V potassium permagate solution was seen in Figure 19. The intense interference to the high wavelength side of the 1 ppm analyte peak is removed. Additionally the analyte peak is more intense than the interfering peak on the low wavelength side due to the reduced background. Hydrochloric acid may also be used as the collecting reagent

The major consideration in cold vapour generation is the removal of the easily reduced precious metals which interfere with the determination by forming amalgams with elemental mercury vapor. These interferents can be easily removed by adsorption onto a carbon column prior to cold vapour generation.

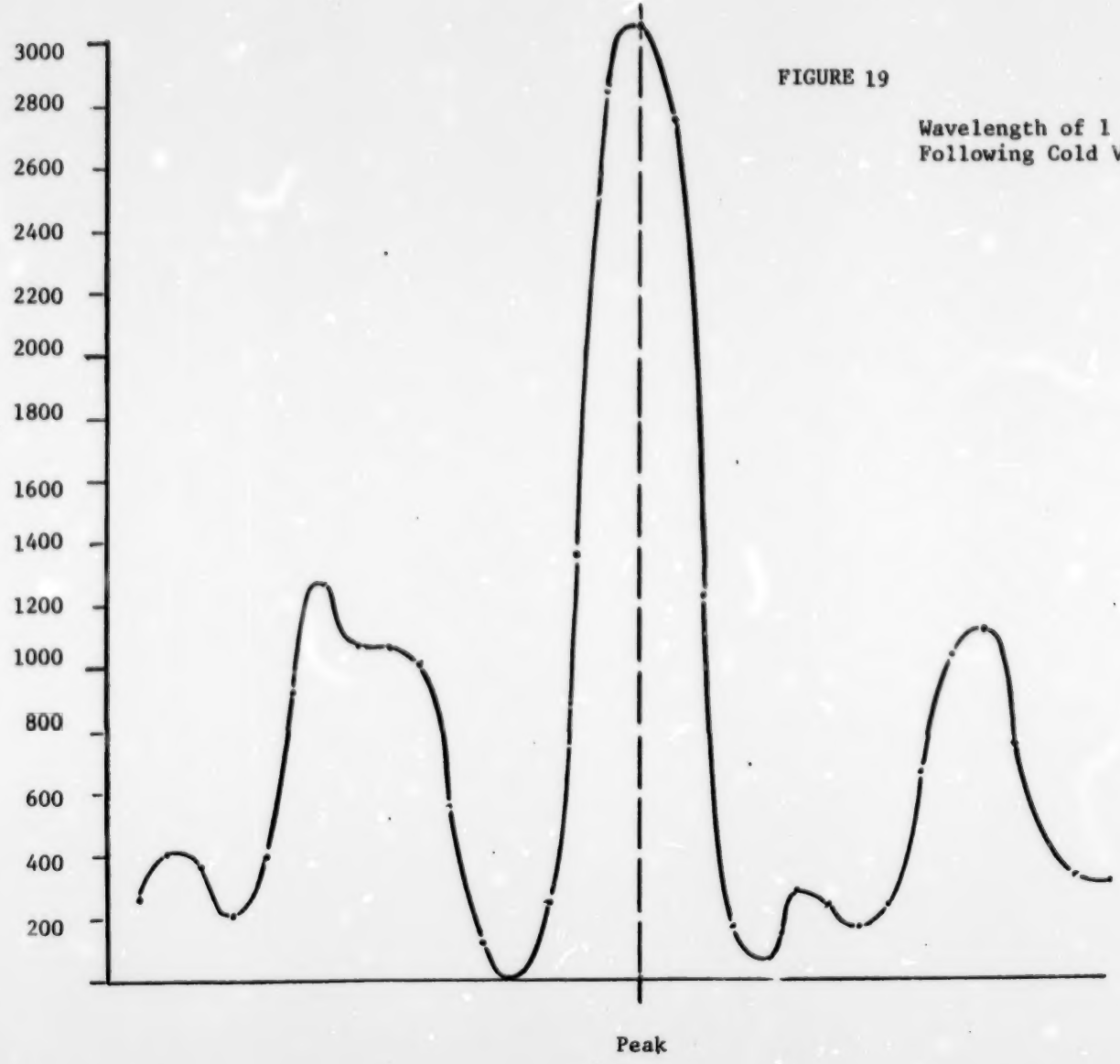


FIGURE 19

Wavelength of 1 ppm Hg
Following Cold Vaporization

Further detailed testwork into the modification of accepted methods to separate and upgrade of arsenic and mercury from milling solutions should lead to the development of a quantitative analytical method suitable for use with emission analysis. The potential definitely exists.

5.0 CONCLUSIONS

Direct analysis of gold milling solutions by Direct Current Plasma Spectroscopy can be completed quickly and accurately for iron, copper, zinc, silver and gold determinations. There are few, if any significant, interelement interferences for these metals which cannot adequately compensated by interferent and matrix matched standards or employment of background correction if necessary. Several useful analyte lines exist for each element which possess spectral and analytical characteristics which fulfill the requirements for accurate analysis of varied metal concentrations in milling solutions. These lines are listed in Table 21.

The stray light from calcium emissions does not pose a serious problem at the concentrations normally encountered in mill solutions. Routine matching of the calcium concentration in the standard matrix, however, is recommended to ensure adequate compensation when and if it is required.

There is evidence of sodium enhancement which also warrants precautionary matrix matching.

The direct analysis of low level mercury and arsenic in gold milling solutions is not recommended. This is a consequence of

TABLE 21

Recommended Analyte Lines for the Analysis of Gold Milling Solutions

Au	242.795 nm
Au	267.595 nm
Ag	328.068 nm
Ag	338.289 nm
Cu	213.598 nm
Cu	224.700 nm
Fe	238.204 nm
Fe	259.940 nm
Zn	202.548 nm
Zn	206.200 nm
As	228.812 nm*
Hg	253.652 nm*

* Not recommended for direct usage in cyanide matrix

the effects of cyanide matrix rather than analytical limitations of the instrument. Emission analysis may be successfully employed following separation and concentration techniques to reduce interferences. This is analogous to the more commonly used atomic absorption methods.

The simultaneous analysis of gold, silver and base metals would present no difficulties providing compatable combinations of anatyte lines were chosen. It must however be kept in mind the simultaneous analysis is inherently a compromise. Operating condition cannot be optimal for each individual element but rather optimized for the particular combination of elements chosen. Similarly, individual background corrections cannot be accommodated in simultaneous analysis. These limitations are of course balanced by the increased sample throughput that is so important in routine analysis. Care must always be taken to ensure that the potentially voluminous data generated is meaningful and correct.

The inclusion of arsenic and mercury in the same simultaneous analysis scheme would be difficult and undesirable due to the difficulties encountered in the cyanide matrix of milling solutions. These elements would best be done sequentially. However, if there was the need to monitor other metals in milling solutions which can form hydrides, such as antimony, selenium etc., these could be determined simultaneously.

In summary, DCP has been shown to be as reliable an analytical

method. Its high sensitivity, precision wide linear dynamic range and freedom from spectral and chemical interferences make it an attractive instrumental method of analysis. It compares very favourably with atomic absorption spectroscopy which is the most commonly used instrumental method for metal analysis. It also compares well with inductively coupled plasma spectroscopy (ICP) but is considerably less expensive to operate.

Analytical wavelengths and background correction, if necessary, must be selected judiciously based on the nature of the sample. Close matrix matching is also desirable as a precautionary step to ensure reliable analytical data. Since analyses are accomplished rapidly and cost effectively, in good agreement with other methods and with respect to metallurgical criteria, the use of direct current plasma spectroscopy should be viewed positively in the mining and metallurgical industries as an attractive alternative.

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APPENDIX I

Analytical Characteristics of Analyte Lines

Au

WAVELENGTH	242.795
ORDER	93
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.03 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.3 to 100 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	1 mg/l

PRECISION (RSD) AT 20 X BEC .76 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Th	5.7
Mn	1.9

Au

WAVELENGTH	267.595
ORDER	84
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.02 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.2 to 100 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	2 mg/l

PRECISION (RSD) AT 20 X BEC .64 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Co	0.6
U	0.8

Au

WAVELENGTH	312.278 nm
ORDER	72
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.3 mg/l
LINEAR DYNAMIC RANGE (LDR)	3 to 100 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	4 mg/l

PRECISION (RSD) AT 10 X BEC .27 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
V	26.7
U	5.0
Th	3.0
Ti	5.4
Cr	1.8
Nb	2.5
Fe	1.1
Mo	1.0

Ag

WAVELENGTH	328.068 nm
ORDER	68
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.01 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.1 to 25 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	0.6 mg/l

PRECISION (RSD) AT 10 X BEC .26 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
U	0.8
Th	0.5

Ag

WAVELENGTH	338.289 nm
ORDER	66
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.02 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.1 to 25 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	0.6 mg/l

PRECISION (RSD) AT 16 X BEC .26 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Ti	1.4
U	1.2

Ag

WAVELENGTH	546.549 nm
ORDER	41
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.1 mg/l
LINEAR DYNAMIC RANGE (LDR)	1 to 300 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	4 mg/l

PRECISION (RSD) AT 5 X BEC .52 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Ti	50
U	40
Mo	20
Nb	13.3
V	11
Ca	6.6
Th	5.0
Cr	2.7

Cu

WAVELENGTH	213.598
ORDER	105
STATE	Ion
PLASMA POSITION	

DETECTION LIMIT	0.04 MG/1
LINEAR DYNAMIC RANGE (LDR)	0.4 to 1000 mg/1
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	3.5 mg/1

PRECISION (RSD) AT 5 X BEC .53 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/1

Cu

WAVELENGTH	224.700
ORDER	100
STATE	Ion
PLASMA POSITION	

DETECTION LIMIT	0.04 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.4 to 1000 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	3.3 mg/l

PRECISION (RSD) AT 5 X BEC .41 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l

Cu

WAVELENGTH	324.754
ORDER	69
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	.002 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.02 to 10 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	0.2 mg/l

PRECISION (RSD) AT 50 X BEC 0.90 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Nb	1.5

Cu

WAVELENGTH	327.396
ORDER	69
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.007 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.07 to 10 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	0.2 mg/l

PRECISION (RSD) AT 50 X BEC .69 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Th	2.9
U	0.7

Cu

WAVELENGTH	521.820 nm
ORDER	43
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.1 mg/l
LINEAR DYNAMIC RANGE (LDR)	1 to 1000 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	2.0 mg/l

PRECISION (RSD) AT 5 X BEC .51 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Ti	16.1
U	5.7
V	5.2
Nb	3.7
Th	2.8
Mo	2.0
Cr	1.6
Al	1.0
Ba	1.0

Fe

WAVELENGTH	238.204
ORDER	94
STATE	Ion
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.01 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.1 to 200 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	.4 mg/l

PRECISION (RSD) AT 20 X BEC .67 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Pt	1.3
Ti	1.1
Au	0.6
Re	0.5
Ni	0.5

Fe

WAVELENGTH	259.940
ORDER	86
STATE	Ion
PLASMA POSITION	

DETECTION LIMIT	0.02 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.2 to 1000 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	.4 mg/l

PRECISION (RSD) AT 12.5 X BEC .50 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Ti	1.0
Au	0.5
U	0.5

Fe

WAVELENGTH	371.994
ORDER	60
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.01 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.1 to 200 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	0.4 mg/l

PRECISION (RSD) AT 20 X BEC 1 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Ti	1.5
U	1.5
Mo	0.7
Nb	0.7
Au	0.6
Ni	0.5
V	0.5

Zn

WAVELENGTH	202.548
ORDER	111
STATE	Ion
PLASMA POSITION	

DETECTION LIMIT	0.01 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.1 to > 100 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	0.8 mg/l

PRECISION (RSD) AT 25 X BEC .35 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l

Zn

WAVELENGTH	206.200
ORDER	109
STATE	Ion
PLASMA POSITION	

DETECTION LIMIT	0.03mg/l
LINEAR DYNAMIC RANGE (LDR)	0.3 to > 100 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	1.0 mg/l

PRECISION (RSD) AT 25 X BEC .53 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l

Zn

WAVELENGTH	213.856
ORDER	105
STATE	Atom
PLASMA POSITION	Optimized by vertical profiling

DETECTION LIMIT	0.03 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.3 to 5 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	0.5 mg/l

PRECISION (RSD) AT 20 X BEC .50 %

INTERFERENT:	EQUIVALENT ANALYTE CONCENTRATION mg/l
Ni	2.6

As

WAVELENGTH	193.696
ORDER	116
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.2 mg/l
LINEAR DYNAMIC RANGE (LDR)	2 to 100 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	9 mg/l

PRECISION (RSD) AT 5 X BEC .98 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Pt	1.3
V	1.0

As

WAVELENGTH	228.812
ORDER	98
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.2 mg/l
LINEAR DYNAMIC RANGE (LDR)	2 to 50 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	15 mg/l

PRECISION (RSD) AT 3 X BEC .91 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Cd	> 20
Pt	9.8
V	1.2
Co	1.1
Ni	1.1

Hg

WAVELENGTH	253.652
ORDER	89
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	0.06 mg/l
LINEAR DYNAMIC RANGE (LDR)	0.6 to > 100 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	2.5 mg/l

PRECISION (RSD) AT 4 X BEC .46 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l
Co	20
Pt	5
Al	2
Fe	0.5

Hg

WAVELENGTH	546.074
ORDER	41
STATE	Atom
PLASMA POSITION	optimized by vertical profiling

DETECTION LIMIT	6.4 mg/l
LINEAR DYNAMIC RANGE (LDR)	10 to 100 mg/l
BACKGROUND EQUIVALENT CONCENTRATION (BEC)	130 mg/l

PRECISION (RSD) AT 1 X BEC .91 %

INTERFERENTS	EQUIVALENT ANALYTE CONCENTRATION mg/l

APPENDIX II

Mass Balance Calculations for Gold Ore Leaching Tests

COMPARATIVE MASS BALANCES

Leach No. 1

Au Assay

Analytical Technique	Filtrate			Wash			Titration			Residue			Total	Calc Head	Assayed Head	Mass
	Vol l.	ppm	mg	vol l.	ppm	mg	vol l.	ppm	mg	wt kg	g/t	mg	mgAu	g/t	g/t	Balance
AA	.770	22.49	17.32	1.000	2.65	2.65	.080	nil	nil	.4858	30.17	14.66	34.63	71.28	64.5	110.5
DCP IMM 3123 nm		--	--		--	--		--	--	--	--	--	--	--	--	---
DCP 242.8 nm	"	27.9	21.48	"	2.39	2.39	"	.33	.03	"	30.17	14.66	38.56	79.37	64.5	123.0
DCP 267.6 nm	"	26.7	20.56	"	2.41	2.41	"	.33	.03	"	30.17	14.66	37.66	77.52	64.5	120.2
DCP MM 242.8 nm	"	24.7	18.79	"	2.80	2.80	"	.35	.03	"	30.17	14.66	36.28	74.68	64.5	115.8
DCP MM 267.6 nm	"	--	--	"	--	--	"	--	--	"	--	--	--	--	--	--
DCP IMM 242.8 nm	"	25.2	19.4	"	2.62	2.62	"	.33	.03	"	30.17	14.66	36.71	75.6	64.5	117.2
DCP IMM 267.6 nm	"	--	--	"	--	--	"	--	--	"	--	--	--	--	--	--

Analytical Technique Legend:

- AA : Atomic absorption
- DCP : Direct Current Plasma, not matrix matched
- DCP MM : Direct Current Plasma, matrix matched
- DCP IMM : Direct Current Plasma, interferent and matrix matched.

COMPARATIVE MASS BALANCES

Leach No. 2

Au Assay

Analytical Technique	Filtrate			Wash			Titration			Residue			Total	Calc Head	Assayed Head	Mass
	Vol l.	ppm	mg	vol l.	ppm	mg	vol l.	ppm	mg	wt kg	g/t	mg	mgAu	g/t	g/t	Balanc
AA	.713			.925			.085			.4906	16.80	8.24				
DCP IMM 3123 nm	"	--	--	"	--	--	"	--	--	"	--	--	--	--	--	--
DCP 242.8 nm	"	112	79.86	"	3.71	3.43	"	6.19	.53	"	16.80	8.24	92.06	187.7	179.3	104.7
DCP 267.6 nm	"	110	78.43	"	3.73	3.45	"	6.40	.54	"	16.80	8.24	90.66	184.8	179.3	103.1
DCP MM 242.8 nm	"	103	73.44	"	4.03	3.73	"	6.72	.57	"	16.80	8.24	85.98	175.3	179.3	97.74
DCP MM 267.6 nm	"	--	--	"	--	--	"	--	--	"	--	--	--	--	--	--
DCP IMM 242.8 nm	"	114	81.28	"	3.72	4.37	"	7.81	.66	"	16.80	8.24	94.55	192.7	179.3	107.5
DCP IMM 267.6 nm	"	--	--	"	--	--	"	--	--	"	--	--	--	--	--	--

Analytical Technique Legend:

- AA : Atomic absorption
- DCP : Direct Current Plasma, not matrix matched
- DCP MM : Direct Current Plasma, matrix matched
- DCP IMM : Direct Current Plasma, interferent and matrix matched.

COMPARATIVE MASS BALANCES

Leach No. 3

Au Assay

Analytical Technique	Filtrate			Wash			Titration			Residue			Total mgAu	Calc Head g/t	Assayed Head g/t	Mass Balance
	Vol l.	ppm	mg	vol l.	ppm	mg	vol l.	ppm	mg	wt kg	g/t	mg				
AA	.405	.76	.308	.990	.25	.248	.735	.11	.081	.5058	tr	tr	.637	1.26	.51	247
DCP IMM 3123 nm		.414	.168		.355	.352		.1	.074		tr	tr	.594	1.17	.51	230
DCP 242.8 nm		.518	.209		.116	.115		.007	.005		tr	tr	.329	.65	.51	128
DCP 267.6 nm		.518	.209		.117	.116		ND	nil		tr	tr	.326	.65	.51	128
DCP MM 242.8 nm		.548	.222		.114	.113		.022	.016		tr	tr	.351	.69	.51	136
DCP MM 267.6 nm		.526	.213		.109	.108		.019	.014		tr	tr	.335	.66	.51	129
DCP IMM 242.8 nm		.567	.230		.113	.112		.017	.013		tr	tr	.355	.70	.51	138
DCP IMM 267.6 nm		.525	.213		.112	.111		.032	.024		tr	tr	.348	.69	.51	135

Analytical Technique Legend:

- AA : Atomic absorption
- DCP : Direct Current Plasma, not matrix matched
- DCP MM : Direct Current Plasma, matrix matched
- DCP IMM : Direct Current Plasma, interferent and matrix matched.

COMPARATIVE MASS BALANCES

Leach No. 4

Au Assay

Analytical Technique	Filtrate			Wash			Titration			Residue			Total	Calc Head	Assayed Head	Mass
	Vol l.	ppm	mg	vol l.	ppm	mg	vol l.	ppm	mg	wt kg	g/t	mg	mgAu	g/t	g/t	Balance
AA	.330	3,29	1.086	1.050	0.80	0.84	.460	0.15	.069	.5057	.24	0.12	2.115	4.18	3.50	119.4
DCP IMM 3123 nm	"	2.682	.885	"	0.099	0.104	"	ND	nil	"	.24	0.12	1.11	2.20	3.50	62.7
DCP 242.8 nm	"	3.10	1.02	"	0.589	0.618	"	.147	.068	"	.24	0.12	1.83	3.62	3.50	103.4
DCP 267.6 nm	"	3.13	1.03	"	.591	.621	"	.120	.055	"	.24	0.12	1.83	3.62	3.50	103.4
DCP MM 242.8 nm	"	3.12	1.030	"	.560	.588	"	.154	.071	"	.24	.12	1.81	3.57	.350	102.2
DCP MM 267.6 nm	"	3.09	1.020	"	.582	.611	"	.151	.070	"	.24	.12	1.82	3.60	3.50	102.9
DCP IMM 242.8 nm	"	3.14	1.04	"	.591	.621	"	.172	.079	"	.24	.12	1.86	3.67	3.50	104.9
DCP IMM 267.6 nm	"	3.00	.986	"	.562	.590	"	.153	.07	"	.24	.12	1.77	3.50	3.50	100.0

Analytical Technique Legend:

- AA : Atomic absorption
- DCP : Direct Current Plasma, not matrix matched
- DCP MM : Direct Current Plasma, matrix matched
- DCP IMM : Direct Current Plasma, interferent and matrix matched.

COMPARATIVE MASS BALANCES

Leach No. 5

Au Assay

Analytical Technique	Filtrate			Wash			Titration			Residue			Total	Calc Head	Assayed Head	Mass
	Vol l.	ppm	mg	vol l.	ppm	mg	vol l.	ppm	mg	wt kg	g/t	mg	mgAu	g/t	g/t	Balanc
AA	1.032	18.45	19.04	1.000	4.06	4.06	.770	.48	.37	.48 2	2.74	1.33	24.80	50.90	53.1	95.9
DCP IMM 3123 nm		16.78	17.32		3.08	3.08		ND	nil		2.74	1.33	21.73	44.60	53.1	84.0
DCP 242.8 nm		20.8	21.47		3.82	3.82		.564	.434		2.74	1.33	27.05	55.52	53.1	104.6
DCP 267.6 nm		20.1	20.74		3.97	3.97		.563	.434		2.74	1.33	26.48	54.4	53.1	102.4
DCP MM 242.8 nm		18.5	19.09		3.82	3.82		.489	.377		2.74	1.33	24.62	50.5	53.1	95.2
DCP MM 267.6 nm		17.2	17.75		3.63	3.63		.517	.398		2.74	1.33	23.11	47.4		89.3
DCP IMM 242.8 nm		18.6	19.20		4.25	4.25		.681	.524		2.74	1.33	25.30	51.94	53.1	97.8
DCP IMM 267.6 nm		17.5	18.06		3.98	3.98		.598	.460		2.74	1.33	23.83	48.91	53.1	92.1

Analytical Technique Legend:

- AA : Atomic absorption
- DCP : Direct Current Plasma, not matrix matched
- DCP MM : Direct Current Plasma, matrix matched
- DCP IMM : Direct Current Plasma, interferent and matrix matched.

COMPARATIVE MASS BALANCES

Leach No. 6

Au Assay

Analytical Technique	Filtrate			Wash			Titration			Residue			Total mgAu	Calc Head g/t	Assayed Head g/t	Mass Balance
	Vol l.	ppm	mg	vol l.	ppm	mg	vol l.	ppm	mg	wt kg	g/t	mg				
AA	.310	3.00	.930	1.010	0.45	.455	0.900	0.17	.153	.5011	1.92	.10	1.64	3.27	3.43	95.3
DCP IMM 3123 nm		--	--		--	--		--	--		--	--	--	--	--	--
DCP 242.8 nm		2.75	.852		.543	.548		.117	.105		1.92	.10	1.61	3.20	3.43	93.4
DCP 267.6 nm		2.72	.840		.566	.570		.107	.100		1.92	.10	1.61	3.22	3.43	93.9
DCP MM 242.8 nm		2.83	.877		.563	.569		.115	.104		1.92	.10	1.65	3.29	--	96.0
DCP MM 267.6 nm		--	--		--	--		--	--		--	--	--	--	--	--
DCP IMM 242.8 nm		2.94	.911		.604	.610		.122	.110		1.92	.10	1.73	3.45	3.43	100.7
DCP IMM 267.6 nm		--	--		--	--		--	--		--	--	--	--	--	--

Analytical Technique Legend:

AA	: Atomic absorption
DCP	: Direct Current Plasma, not matrix matched
DCP MM	: Direct Current Plasma, matrix matched
DCP IMM	: Direct Current Plasma, interferent and matrix matched.

COMPARATIVE MASS BALANCES

Leach No. 7

Au Assay

Analytical Technique	Filtrate			Wash			Titration			Residue			Total mgAu	Calc Head g/t	Assayed Head g/t	Mass Balance
	Vol l.	ppm	mg	vol l.	ppm	mg	vol l.	ppm	mg	wt kg	g/t	mg				
AA	.403	5.05	2.04	1.000	1.00	1.00	.850	.20	.17	.500	.17	.085	3.30	6.59	5.01	132
DCP IMM 3123 nm	"	--	--	"	--	--	"	--	--		--	--	--	--	--	--
DCP 242.8 nm	"	4.29	1.73	"	.779	.779	"	.091	.077	.500	.17	.085	2.67	5.34	5.01	106.6
DCP 267.6 nm	"	4.39	1.77	"	.812	.812	"	0.68	.058	.500	.17	.085	2.73	5.45	5.01	108.8
DCP MM 242.8 nm	"	4.52	1.82	"	.847	.847	"	.124	.105	"	.17	.085	2.86	5.71	--	114.1
DCP MM 267.6 nm	"	--	--	"	--	--	"	--	--	"	--	--	--	--	--	--
DCP IMM 242.8 nm	"	4.53	1.83	"	.847	.847	"	.127	.108	.500	.17	.085	2.87	5.74	5.01	114.6
DCP IMM 267.6 nm		--	--		--	--	"	--	--	"	--	--	--	--	--	--

Analytical Technique Legend:

AA : Atomic absorption
DCP : Direct Current Plasma, not matrix matched
DCP MM : Direct Current Plasma, matrix matched
DCP IMM : Direct Current Plasma, interferent and matrix matched.